Correlating Electrolyte Inventory and Lifetime of HT-PEFC by Accelerated Stress Testing

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Phosphoric acid electrolyte evaporation in a polybenzimidazole based high temperature polymer electrolyte fuel cell is analyzed as a function of reactant gas stoichiometry and temperature. Based on these results a phosphoric acid vapor pressure curve is derived to predict the fuel cell lifetime with respect to electrolyte inventory. The predicted fuel cell life was validated by means of an accelerated stress test. Additionally, the correlation between electrolyte inventory and fuel cell performance was investigated by recording H2/air and H2/O2 polarization curves during the course of the stress test to gain insight into the relation between acid inventory and the different degradation modes.

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Manuscript submitted July 21, 2015; revised manuscript received September 1, 2015. Published September 11, 2015.

High-temperature polymer electrolyte fuel cells (HT-PEFC) have the potential to become an important technology for small scale heat and power (CHP) applications. However, today, fuel cell based CHP applications are dominated by low-temperature PEFC (LT-PEFC), even though the possibility to sustain high CO levels of up to 3% and even full integration from cathode to anode under high current operation.4 This loss by evaporation and migration is exclusive to HT-technology and a consequence of additional gas humidification, and high system efficiencies are ideal properties of HT-PEFC for stationary CHP applications.

Fuel cell durability, efficiency and cost are essential factors for commercialization. Durability is mainly determined by membrane electrode assembly (MEA) degradation. Amongst other degradation modes that HT-PEFCs share with low temperature PEFC, electrolyte loss by evaporation and migration is exclusive to HT-technology and a limiting factor for CHP applications. We have recently demonstrated that PBI based membrane systems exhibit extensive electrolyte migration from cathode to anode under high current operation.4 This was attributed to the high mobility of free hydrogen phosphate anions which carry part of the ionic current. While this work focuses on phosphoric acid loss by evaporation and its implication on lifetime and fuel cell performance, it cannot be excluded that the high PA mobility has an effect on electrolyte evaporation as it can influence the PA resupply and saturation of the electrodes.

With respect to electrolyte evaporation, the phosphoric acid vapor pressure below temperatures of 300 °C is extremely low, nevertheless it is expected to be significant considering the targeted lifetime of 50,000 h for CHP systems set out by the US Department of Energy (DOE) for 2015.5 Up to now, no literature data is available for the vapor pressure of phosphoric acid for temperatures below 200 °C.6,7 Determining a phosphoric acid vapor pressure curve at the temperatures of interest for fuel cell operation (160–190 °C) is a tedious task, due to the low phosphoric acid concentration in the gas phase and the accompanied analytical measurement complexity. Furthermore, phosphoric acid, being a mixture of water, ortho- and polyphosphoric acid, changes concentration and chemical structure10 with changing temperature and water partial pressure. The partial pressure of water over phosphoric acid needs to be adjusted to keep the acid concentration constant when trying to determine the vapor pressure curve. In a fuel cell, this task is even more complicated considering that water vapor pressure changes with current density, temperature and stoichiometry. Additionally, in fuel cells of technical size, gradients in concentration, temperature and gas saturation occur in through- as well as in-plane direction. Hence, predicting the lifetime of electrolyte in a technical HT-PEFC would require measuring a large parameter space.

As alternative instead of determining the phosphoric acid vapor pressure, the phosphoric acid loss rates can be measured for an operating HT-PEFC. However, literature data3,11 is rare and persistently given in mass per active area for a given temperature, stoichiometry and current density. Consequently, a change in operating conditions or even fuel cell size might result in vastly different electrolyte loss rates. The existing data base is not sufficient for lifetime predictions.

The aim of this work is therefore to correlate operating conditions and operating time with electrolyte inventory to predict fuel cell lifetime. Therefore, the focus is set on clarifying the effects of gas flow rate, cell temperature and current density on the phosphoric acid loss by evaporation. PA losses are evaluated by condensation at the outlet of 45 cm² cells and the loss rates are validated with an accelerated stress test at 190 °C where the influence of phosphoric acid inventory on different performance loss mechanisms is investigated.

Experimental

General.— All experiments were carried out with BASF Celtec membrane electrode assemblies (MEA). These MEA consist of a H3PO4 doped polybenzimidazole (PBI) membrane with an acid loading of 36 mgH3PO4 cm⁻² ± 6% and a PA to PBI molar ratio of 33 ± 2. The acid loading values and molar ratios were determined before MEA assembly by measuring the acid content of several pristine membranes by ion chromatography (IC). The thickness of the membrane after cell assembly is approximately 100 μm.4 During MEA preparation PA gets partially transferred to the electrodes and the membrane acid content defines the MEA beginning of life (BoL) acid content. The electrodes consist of Pt/Vulcan XC-72 supported platinum catalyst with a loading of 1 mgPt cm⁻² on anode and cathode, respectively, coated onto SGL 38 carbon paper gas diffusion layers (GDL) including a microporous layer.

For cell assembly, additional Kapton sub-gaskets are used on cathode and anode, which are partially overlapping with the membrane and electrode.5,12 Additional 320 μm thick perfluoroalkoxyalkane (PFA) sealings on top of the sub-gaskets act as a hard stop and define GDL compression by constant gap.13 All tests were performed on 45.2 cm² active area single cell setups using pyrolytically surface treated and sealed graphite flow fields (proprietary surface treatment by POCO Graphite, USA). The flow field channel structure consists of a serpentine channel geometry (1.2 mm width and 2.0 mm depth) with two and three channels on anode and cathode, respectively. Cells were operated in co-flow with dry hydrogen and air unless stated otherwise. Break-in was performed for 48–120 h at 160 °C and stoichiometries of λH₂ = 1.2 and λair = 2.0.

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Phosphoric acid loss.—In order to determine the phosphoric acid loss during fuel cell operation, the phosphoric acid/water vapor mixture in the exhaust gas stream of anode and cathode was condensed by passing each stream through water in a polypropylene bottle. The sample containers were emptied every 24–300 h after flushing the PFA flange and tube between sample container and fuel cell with 50 ml of deionized water. Therefore, all phosphoric acid that condensed between cell and sample container is collected as well. The concentration of the water/phosphoric acid mixture was subsequently analyzed by ion chromatography (IC) (Metrohm 882 Compact IC plus System; Metrosepp A Supp 5 150 anion separation column). The IC system measures the HPO$_4^{2-}$ concentrations in the range of 1–20 ppm (ng L$^{-1}$) with an accuracy of ±1.5%, determined by periodically measuring standards. The loss rate of H$_3$PO$_4$ from the MEA can be calculated as follows:

$$H_3PO_4 	ext{ loss rate} = c_{H_3PO_4} \cdot V_{sample} \cdot \left( \frac{M_{H_3PO_4}}{M_{HPO_4^2-}} \right) \cdot (A \cdot t)^{-1}$$

where the H$_3$PO$_4$ loss rate is given in ng cm$^{-2}$ h$^{-1}$, $c$ is the HPO$_4^{2-}$ concentration in ng L$^{-1}$, $V_{sample}$ the volume of liquid in the plastic bottle determined by weighting ($\bar{m}_{H_3PO_4} = 0.998$ g cm$^{-3}$ at 20℃), $M$ the molar mass ($M_{H_3PO_4} = 98$ g mol$^{-1}$; $H_3PO_4$ = 96 g mol$^{-1}$; the term corrects for the difference in molar mass between the two species), $A$ the active area of the fuel cell and $t$ the time the bottle was connected to the fuel cell. The downside of this acid loss rate representation is that it does not directly correlate the acid loss with gas volume flow. Therefore, a different representation was chosen where the PA loss is expressed as a PA concentration in the gas leaving the anode and cathode, respectively, as given in Equation 2:

$$c_{H_3PO_4,ls} = H_3PO_4 	ext{ loss rate} \cdot \frac{A}{V(T, j, \lambda)} \tag{2}$$

H$_3$PO$_4$ concentration is typically in the ppt (ng L$^{-1}$) range, $V$ is the volumetric outlet gas flow in L h$^{-1}$ as a function of fuel cell operating temperature $T$, gas stoichiometry $\lambda$ and current density $j$ and is calculated from the ideal gas and Faraday’s laws with the assumption that all produced water vapor is leaving the cell on the cathode side. Error bars in the plots indicate the variation of phosphoric acid evaporation during the measurement cycles. Phosphoric acid evaporation rates of the anode are not presented for $\lambda_{\text{Anode}} \leq 3.6$, due to detection limits of the IC. Standard conditions (0℃, 101,325 Pa) are indicated for gas volumes by NL. Otherwise, the volume of gas is calculated at the respective temperature.

Based on the PA content in the gas, a vapor pressure curve can be derived using Antoine’s equation. The vapor pressure of phosphoric acid is calculated at the respective temperature $T$ according to:

$$p_{H_3PO_4} = c_{H_3PO_4,v} \cdot \frac{RT}{M_{H_3PO_4}} \tag{3}$$

In this equation $p_{H_3PO_4}$ is the vapor pressure of phosphoric acid and R the ideal gas constant. The Antoine Equation is then given as:

$$\log p_{H_3PO_4} = A - \frac{B}{(C + T)} \tag{4}$$

where A, B and C are fitting parameters and T is the temperature of the fuel cell in Kelvin. This equation assumes a constant heat of vaporization, reducing its validity to a narrow temperature range.

Accelerated stress test (AST).—After a break-in period of 120 h at 160℃, the fuel cell was operated at 190℃, 0.2 A cm$^{-2}$ and gas flow rates of 100 NL h$^{-1}$/50 NL h$^{-1}$ on cathode/anode side. The challenge of an AST is to choose operating parameters that trigger only a single degradation mode, in this case electrolyte evaporation, and minimizing all other degradation effects, c.f. carbon corrosion, membrane pinhole formation, GDL electrode flooding with PA, catalyst particle detachment and agglomeration. Since this is realistically not possible, a characterization method is necessary to gain insight into the different cathode degradation modes. Therefore, polarization curves with H$_2$-air ($\lambda_{H_2}/\lambda_{air} = 1.2/2$) and H$_2$-O$_2$ ($\lambda_{H_2}/\lambda_{O_2} = 1.29/5$) were recorded at the beginning of life and during the course of the experiment in time intervals of 200–360 h. Ohmic cell resistances are measured with 1 kHz AC impedance measurements (Hoechler & Hackl 80A electronic load with integrated sine wave generation).

### Determination of voltage loss terms.—A brief explanation of the different voltage loss terms and how to retrieve them is given here. A more extensive explanation can be found elsewhere. It was previously shown that all kinetic and mass transport losses of the hydrogen electrode can be neglected. Therefore, the cell voltage $E_{cell}$ can be described according to Equation 5:

$$E_{cell} = E^0(\bar{p}_{H_2, O_2, H_2O, T}) - \eta_{O_2RR} - \eta_{\text{mass}} - \eta_{IR} \tag{5}$$

where $E^0$ is the equilibrium potential at a given temperature and gas partial pressures, $\eta_{O_2RR}$ the oxygen reduction reaction overpotential, $\eta_{\text{mass}}$ the mass transport overpotential induced by O$_2$ transport through the GDL and catalyst layers and $\eta_{IR}$ the voltage loss due to ohmic resistance of the cell. $E^0(\bar{p}_{H_2, O_2, H_2O, T})$ is given by:

$$E^0(\bar{p}_{H_2, O_2, H_2O, T}) = -\frac{\Delta G(T,p)}{2F} + \frac{2.303 RT}{2F} \log \left( \frac{\bar{p}_{H_2O_2, T}}{\bar{p}_{H_2O}} \right) \tag{6}$$

where $\Delta G(T,p)$ is the Gibbs free energy of formation at a given temperature and a pressure of 101,325 Pa for gas phase water. The second term corrects the reversible potential for the mean gas partial pressures of hydrogen, oxygen and water.

By correction of the IR drop and assuming a purely kinetic controlled polarization curve when using pure oxygen as the cathode gas, equation 5 can be simplified to:

$$E_{cell,IR-free} = E^0(\bar{p}_{H_2, O_2, H_2O, T}) - \eta_{O_2RR} \tag{7}$$

The oxygen reduction reaction overpotential can now be calculated as the difference between the reversible potential $E^0$ and the measured ohmic drop corrected oxygen polarization curve.

In order to calculate the mass transport overpotential, a theoretical Tafel line for air polarization has to be calculated. The difference between the measured air polarization and this theoretical line can then be attributed to mass transport losses. The theoretical air polarization curve is shifted to lower potentials by the difference in reversible potential between the average oxygen partial pressures of air and oxygen operation as given by:

$$\Delta E_{O_2-air} = \Delta E^0 + b \log \left( \frac{p_{O_2, air}}{p_{O_2}} \right) \tag{8}$$

In this equation $\Delta E^0$ is the difference in reversible potential between air and oxygen, $b$ the Tafel slope and $\gamma$ the reaction order ($\gamma = 0.52 \pm 0.05$). The measured Tafel slope in the performed experiments is in the order of 105 ± 5 mV/decade, which is close to the theoretical value of 92 mV/decade (= 2.303 RT/F). Deviations from this ideal value can be attributed to non-ideal design of the electrodes.

For better comparison of the measured data, the different overpotentials are given as difference to the values at BoL after break-in according to:

$$\Delta \eta_{O_2RR} = \eta_{O_2RR, BoL} - \eta_{O_2RR, BoL} \tag{9}$$

$$\Delta \eta_{O2RR, mass} = \eta_{\text{mass, BoL}} - \eta_{\text{mass, BoL}} \tag{10}$$

$$\Delta \eta_{IR} = \eta_{IR, BoL} - \eta_{IR, BoL} \tag{11}$$

### Results and Discussion

In this section phosphoric acid loss rates of BASF Celtec MEA as a function of temperature and gas stoichiometries are presented. Based on these results, vapor pressure curves are derived, which give the
Phosphoric acid content in the exhaust gas stream of the cathode as a function of temperature and gas flow rate. 

Figure 1. Phosphoric acid content in the exhaust gas stream of the cathode as a function of temperature and gas flow rate.

Phosphoric acid content in the exhaust gas stream of the anode as a function of temperature and gas flow rate. 

Figure 2. Phosphoric acid content in the exhaust gas stream of the anode as a function of temperature and gas flow rate.

Table I. $H_3PO_4$ concentration in the off-gas of cathode and anode for different temperatures.

| Temperature [$^\circ$C] | Current density [Acm$^{-2}$] | $c_{H_3PO_4}$ in air [ng L$^{-1}$] | $c_{H_3PO_4}$ in $H_2$ [ng L$^{-1}$] |
|-------------------------|-----------------------------|----------------------------------|-----------------------------------|
| 160                     | 0.2                         | 411 ± 23                         | 325 ± 32                          |
| 170                     | 0.2                         | 822 ± 41                         | 777 ± 54                          |
| 180                     | 0.2                         | 1842 ± 72                        | 1630 ± 140                        |
| 190                     | 0.2                         | 2497 ± 108                       | 2618 ± 135                        |

possibility to predict the electrolyte retention time within the MEA over a wide range of operating parameters. Finally an accelerated stress test is implemented to correlate electrolyte inventory with fuel cell lifetime and performance.

Phosphoric acid loss.— In Figures 1 and 2 and Table I phosphoric acid concentration in the off-gas stream of cathode and anode is presented as a function of temperature from 160–190°C and fuel cell inlet gas flow rates. It can be seen that in the temperature range of 160–180°C the PA content in the gas scales exponentially with temperature but is independent (within measurement accuracy) of flow rate or current density as additionally pointed out in Table II for measurements at 160°C. It should also be noted that a change in stoichiometry on only anode or cathode does not influence the electrolyte content in the gas phase, i.e., doubling the flow rate on the anode has no influence on the phosphoric acid loss rate of the cathode and vice versa. Hence, the water drag reported for HT-PEFC can be neglected as influencing factor for the studied parameter range.

At first sight, these results are unexpected considering the fact that the phosphoric acid vapor pressure is a function of concentration and a change in gas stoichiometry induces a change in concentration due to a change in water partial pressure. Additionally, high current densities induce extensive phosphoric acid migration within the fuel cell and are, at least locally, changing the electrolyte concentration. We attribute this insensitivity of the PA content to the gas volume flow to a negligible change in latent heat of vaporization for the concentrations compared to the measurement accuracy. Furthermore, the residence time of gas within the fuel cell is high enough to fully saturate the gas with phosphoric acid independent of electrolyte concentration and, hence, the phosphoric acid gas content scales solely with the outlet gas volume. Consequently, evaporation rate or transport limitation (diffusive gas phase transport through the porous transport medium) can be neglected for the temperature range of 160°C to 180°C and stoichiometries of up to $\lambda_{air}/\lambda_{stoich}$ 8/8 at 0.2 A cm$^{-2}$.

At 190°C the evaporation rates still increase compared to lower temperatures but the PA content in the gas of the cathode deviates significantly for gas flows of 18 NL h$^{-1}$ and 54/90 NL h$^{-1}$. On the anode side, the effect is also present, although less pronounced. It has been shown that gas crossover between adjacent channels in a serpentine flow field occurs when gas velocities increase beyond a certain threshold. The reason for this is a pressure difference between adjacent channels and consequently the residence time of gas within the fuel cell decreases at higher flow rates. This might lead to insufficient time for the gas to saturate with electrolyte vapor. Since the PA gas concentration increases roughly exponentially (cf. Figures 1–4) and the residence time decreases linearly with the volumetric gas flow rate, a limitation by diffusive gas phase transport or evaporation rate becomes apparent at high temperatures (≥190°C) and stoichiometries $\lambda_{air}$ ≥ 2.

A comparison of PA gas content for a phosphoric acid fuel cell (PAFC) and the cathode gas content of a HT-PEFC is shown in Figure 3. In the range of 160–180°C the linear increase (in the semilog plot) and overlapping values in PA gas content for both technologies further confirm the suggested PA loss by vapor saturation. Additionally, at 190°C the PA vapor concentration for the HT-PEFC shows a distinctive deviation from the linear vapor saturation behavior. In Figure 4 the vapor pressure for cathode and anode is plotted for the same gas inlet flowrates and current density (18 NL h$^{-1}$/13.6 NL h$^{-1}$ cathode/anode; 0.2 A cm$^{-2}$) as a function of temperature. Using Antoine’s equation, a vapor pressure curve for cathode and anode can be calculated, which is indicated by the straight lines in Figure 4. The derived fitting parameters are given in Table III. It becomes apparent that the vapor pressure of $H_3PO_4$ in the fuel cell gas outlets of anode and cathode varies noticeably in the range 160–180°C while the two values fall together at 190°C. In the temperature range of 160–180°C, anode and cathode gas streams are both saturated with PA and no transport or evaporation rate limitation can be observed as discussed above. Consequently only the 160–180°C values are used to derive the fitting parameters for Antoine’s equation. We can only speculate about the reason behind the difference in vapor pressure for

Table II. $H_3PO_4$ concentration in the off-gas of cathode and anode for 0.2 and 0.8 A cm$^{-2}$ at constant gas flow rates.

| Temperature [$^\circ$C] | Current density [Acm$^{-2}$] | $\lambda_{air}/V$ [NL h$^{-1}$] | $\lambda_{stoich}/V$ [NL h$^{-1}$] | $c_{H_3PO_4}$ in air/H$_2$ [ng L$^{-1}$] |
|-------------------------|-----------------------------|-------------------------------|---------------------------------|-----------------------------------|
| 160                     | 0.2                         | 8/72                          | 8/30.2                          | 397 ± 14 / 339 ± 27               |
| 160                     | 0.8                         | 2/72                          | 2/30.2                          | 424 ± 9 / 312 ± 18               |
Figure 3. PA content in the exhaust gas stream of HT-PEFC (cathode gas stream $\lambda_{air} = 2$) and PAFC (data reproduced from Ref. 24) as a function of temperature.

Figure 4. Vapor pressure curve of H$_3$PO$_4$ in the gas outlet of anode and cathode of a 45.2 cm$^2$ active area single cell and $\lambda_{H_2}/\lambda_{air} = 3.6/2$. The fitting is indicated by the lines and is performed for temperatures from 433 to 453 K. Squares indicate measured cathode values and circles measured anode values.

cathode and anode. It might be caused by a local temperature sink in the endplate of the anode, causing PA to condense before it reaches the fuel cell outlet. Another explanation could be a non-ideal behavior of the carrier gas – PA vapor mixture which leads to a vapor pressure depression effect. The measured vapor pressure values at 190°C for anode and cathode are significantly lower than predicted by the Antoine fit, presumably due to the presence of transport or evaporation rate limitations already at the low flow rates of 18/13.6 NL h$^{-1}$.

In Figure 5, a lifetime prediction with respect to electrolyte inventory was made by applying the derived Antoine fit for 160–180°C and a stoichiometry of $\lambda_{H_2}/\lambda_{air} = 3.6/2$. Since the acid loading ($\approx$36 mgPA cm$^{-2}$) of the MEA is known, a total mass of phosphoric acid in the MEA can be calculated. Assuming a constant phosphoric acid evaporation rate throughout the lifetime of the fuel cell, the time for total acid loss can be calculated. It should be noted that the results yield the highest accuracy for current densities between 0.2 and 0.8 A cm$^{-2}$ at 160°C and 0.2 – 0.6 A cm$^{-2}$ at 170 – 180°C. Values for higher current densities were extrapolated and therefore mass transport or evaporation limitation cannot be excluded. It is expected that the results can be transferred to single cells or even stacks of similar or bigger size. The results can be compared to the DOE’s$^5$ 50,000 operating hours requirement of medium sized CHP systems. The DOE’s failure characteristic is a 10% loss of electrical performance and hence, the plotted time to 0% PA content is therefore certainly an overestimation. Additionally, as will be shown later, the phosphoric acid within the membrane is very mobile, making it necessary to also account for the phosphoric acid in the membrane underneath the sub-gasket, outside of the active area. With the present MEA design, this increases the absolute phosphoric acid amount of the MEA by about 13%. Nevertheless, the examined HT-PEFC MEA is highly unlikely to reach the desired lifetime for temperatures $\geq$170°C. Even at 160°C any operating point beyond 0.2–0.4 A cm$^{-2}$ significantly increases the risk of failing the DOE requirement. With these results in mind, the question then arises as to what extent phosphoric acid loss from the MEA degrades performance. Therefore, an accelerated stress test was carried out, which is discussed in the next section.

**Table III. Fitting parameters for the Antoine equation (Equation 4).**

|      | A   | B   | C       |
|------|-----|-----|---------|
| Cathode | 5.09 | 1201.00 | -260.44 |
| Anode  | 2.88 | 543.21 | -320.10 |

*Accelerated stress test.* — For interpretation of the results in the previous section, an accelerated stress testing protocol was implemented to analyze the influence of electrolyte loss on actual HT-PEFC lifetime and performance. In order to maximize phosphoric acid loss and minimize measurement time, a temperature of 190°C with high hydrogen and air flow rates of 50 and 100 NL h$^{-1}$, respectively, corresponding to stoichiometries of $\lambda_{H_2} = 13.2$ and $\lambda_{air} = 11$, was chosen. The voltage profile including the measured high frequency resistance and PA loss from the MEA is shown in Figure 6. During the first 2000 h of operation an approximately linear voltage degradation of 41 $\mu$V h$^{-1}$ was observed. Up to 2000 hours, the non-linear increase of the HFR is too weak to dominate voltage degradation and indicates overlapping degradation modes. Only after 2000 hours the exponential increase in ohmic resistance ultimately leads to fuel cell failure.
after 2830 h. Interestingly, the measured phosphoric acid loss rate from the cell did not change throughout the test, suggesting a negligible influence of the polymer–electrolyte interaction down to low PA doping levels. At end of life (EoL) a circular part of the MEA was cut out and the phosphoric acid left was determined to be $17 \pm 1\%$ of the initial content, which is equivalent to an acid loading of $4.7 \pm 0.7$ mgH$_3$PO$_4$ cm$^{-2}$. The remaining amount of acid, measured from evaporated PA was calculated to be $13 \pm 6\%$, confirming the accuracy of the determination of evaporated PA. It is important to note, that the overlapping part of the membrane which was partially clamped in between the sub-gaskets was also taken into account for the total phosphoric acid amount. This was verified by measuring the PA amount of a piece of membrane clamped in between the sub-gaskets at EoL and comparing it to a part of the MEA from the active area. Both pieces exhibit almost identical PA loadings. We therefore conclude that PA in these membranes is very mobile and at EoL most of the remaining electrolyte can be found within the membrane.

The contribution of the different overpotentials on cell performance loss was determined by measuring separate H$_2$/Air and H$_2$/O$_2$ polarization curves. The procedure for evaluation of the different contributions is described in the Experimental section. The split into ohmic, mass transport and ORR overpotential contributions of the total voltage degradation is plotted for 0.2 and 0.8 A cm$^{-2}$ in Figure 7. Voltage degradation can be split into three regions as indicated in Figures 6 and 7.

In region I the oxygen reduction overpotential at operating points of 0.2 and 0.8 A cm$^{-2}$ increases by about 30 mV and becomes the dominating factor at low current densities. It has been pointed out that this decrease in cathode kinetics during the first 500–1000 h can mainly be attributed to platinum particle growth. An increase in oxygen reduction overpotential of 30 mV equals to a reduction in electrochemical active surface area (ECSA) by approximately 50%. The mass transport overpotential also increases in region I and is the major contributor to performance loss at high current density. This degradation effect can most probably be attributed to changes in hydrophobicity of the catalyst layer, resulting in higher saturations with PA effectively increasing mass-transport resistances. The loss of ECSA could potentially also be attributed to a deficiency of electrolyte within the electrodes, effectively decreasing the three phase boundary but the high PA mobility and strong increase of $\Delta\eta_{\text{mass}}$ render this highly unlikely. Performance loss due to increases in ohmic resistance can be neglected during the first 1200 h, leading to the conclusion that a loss of almost 40% PA (c.f. Figure 6) is of no concern for this kind of MEA.

Region II is characterized by a stabilization of oxygen reduction and mass transport overpotentials at low and high current densities. Ohmic resistance on the other hand increases strongly from 1200 operating hours onward. In the constant gap set-up this can potentially be attributed to an increase in contact resistance concomitant with an increase of proton resistance of the membrane due to loss of electrolyte.

In region III, fuel cell degradation is again mainly driven by the evaporation of phosphoric acid as can be seen by a strong increase in $\Delta\eta_{\text{IR}}$. This corresponds well to literature data where a strong decrease in ionic conductivity occurs for PPA processed m-PBI membranes for PA/PBI ratios $\approx$ 8–10. Furthermore, at 2300 h, mass transport improves slightly at 0.2 A cm$^{-2}$ and significantly at 0.8 A cm$^{-2}$. This can be interpreted as evaporation of excess PA in the electrodes and consequently easier access for reactant gas to the catalyst layer. Increased loss of PA from the electrodes and reduction of the three phase boundary area then causes a strong increase in oxygen reduction reaction overpotential. This is promptly followed by the fuel cell failure after 2830 h.

The final PA/PBI ratio of $\approx$ 5, is, according to literature, an optimal compromise between conductivity and mechanical stability for film casted m-PBI membranes. Hence, mechanical failure or insufficient proton conductivity can theoretically be excluded as failure mode. It is therefore hypothesized that fuel cell failure is either due to complete loss of PA from the electrodes or due to catalyst layer detachment. If only ohmic losses due to electrolyte evaporation are considered,
a phosphoric acid loss of 65%–70% at 0.8 A cm\(^{-2}\) and 75–80% at 0.2 A cm\(^{-2}\) can be tolerated before the DOE threshold of 10% performance loss occurs. A more sophisticated compression setup, compensating thickness loss of the MEA, might even push these limits further by reducing contact resistance and catalyst layer detachment effects. The predicted lifetimes in Figure 5 need to be reduced by about 20% (at the given stoichiometry) to give realistic lifetimes with respect to acid inventory for the tested and highly doped (\(\approx 40 \) PA/PBI) MEAs. PBI film casted membranes with a much lower doping level enhanced cooling reduces the reactant temperature by 20–40\(^\circ\)C. This was realized by implementing a condensation of phosphoric acid in phosphoric acid fuel cells (PAFC). A more sophisticated compression setup, possibly due to platinum particle growth and changes in hydrophobicity of the catalyst layer. Subsequently, phosphoric acid loss induced increased ohmic losses concomitant with kinetic and mass transport improve-
ments, possibly due to advantageous electrolyte distribution within the electrodes. The final fuel cell failure was attributed to electrolyte starvation within the electrodes, caused by insufficient resupply of PA from the membrane or even catalyst layer detachment.

If only ohmic losses are considered for PA loss induced degradation, an acid loss of 65–80% can be tolerated before reaching DOE’s 10% performance loss threshold. In conclusion, to achieve lifetime requirements also at temperatures above 160\(^\circ\)C and high current densities, an advanced phosphoric acid electrolyte management seems inevitable.

Acknowledgments

Financial support from BASF SE, software and electronic support by T. Gloor and support with the test bench by T. Engl are gratefully acknowledged.

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