An increasing use of fuel cell electric vehicles involves the need to understand their behavior at low ambient temperatures as well as under cold-start conditions. Here commercial 60 wt.% Pt/C catalyst (HiSPEC9100) was studied in the temperature range 0–20°C using rotating disc electrode (RDE) setup and single cell inside a climate chamber. RDE measurements of oxygen reduction reaction (ORR) activity revealed decreasing activity with lower temperatures as well as activation energies and reaction mechanisms comparable to high temperature studies. Catalyst degradation was significantly lower at lower temperatures, which was confirmed by CO stripping. The increase of the specific ORR activity after degradation measurements is discussed in terms of morphological changes of the Pt particles. Single cell tests confirmed significant performance reduction at lower temperatures. Furthermore, measurements at different power densities were conducted to evaluate heating and flooding effects.

Keywords: Carbon Corrosion, Catalyst Degradation, Cold-Start, Electrocatalysis, Fuel Cells, Oxygen Reduction Reaction, Platinum, Temperature Dependence

1 Introduction

Even though power generation from H 2 and O 2 was already successfully done in 1839 [1, 2], only recently advancements in fuel cell technology have led to the release of commercially available fuel cell electric vehicles (FCEVs), such as the Toyota Mirai or Hyundai Tucson. While batteries become larger and heavier with higher payload, fuel cells provide the ability to scale up power delivery for minimized increased size and weight [3]. Hence, fuel cell technology is also in R&D focus for heavy (or medium) duty trucks, even though battery powered electric vehicles are more common until now. So called fuel cell electric trucks (FCETs) were demonstrated by various companies, such as Toyota or Nikola.

For FCEVs as well as FCETs, fuel cell performance and behavior at low ambient temperatures (0–20°C) is a crucial criterion especially in terms of cold-start and driving short distances. Most published literature targeting cold start in proton exchange membrane (PEM)-fuel cells are focusing on thermal and water management [4]. For example Yan et al. [5] studied the cold start behavior and fuel cell performance using 25 cm² single cells at climate chamber temperatures between −15 and 80°C. A successful self-start was possible down to −5°C temperature at current densities up to 200 mA cm⁻², if the cell was purged and insulated properly. At −10°C higher air stoichiometries, higher feed gas temperatures and lower current densities (100 mA cm⁻²) were needed to perform a successful startup. Too slow heating of the cell and freezing of the product water were considered as reasons for failure of the cell.

Nevertheless, little is known about the temperature impact on the catalyst in this temperature region and its relevance on single cell and stack level. To the best of our knowledge, the only study paying attention to this problem using rotating disc electrode (RDE) was conducted by Zalitis et al., who investigated the hydrogen oxidation reaction (HOR) in a range from 5 to 60°C [6]. In comparison to the HOR in PEM-fuel cells the oxygen reduction reaction (ORR) occurring on the cathode side contributes to a major part to the overpotential in the total cell voltage due to its sluggish kinetics [7]. For this reason the investigation and optimization of the ORR has...
drawn much focus in the field of fuel cell research in recent years. Yet, there is plenty of published literature of ORR kinetics in the temperature range above ambient temperature [8–12], literature concerning ORR kinetics below 20°C is sparse. For example Hou et al. compared ORR kinetics by electrochemical impedance spectroscopy (EIS) before and after freezing the cell. No change of ORR mechanism was found after exposing the cell in 8 freeze/thaw cycles [13].

Herein, the focus will be on rotating disc electrode (RDE) investigations of the ORR on commercial Pt catalyst (60 wt.% Pt/C, HiSPEC9100, Johnson Matthey) as well as carbon degradation between 0 and 20°C. Our previous investigations of carbon corrosion at temperatures higher than 23°C in PEMFCs using a differential electrochemical mass spectrometry (DEMS) setup show strong temperature dependence [14]. To expand the relevant temperature range for automotive applications, studies on the durability of the catalyst support were carried out also on the RDE level in the temperature range 0–20°C.

Moreover, fundamental feasibility of cold starts on single cell level was investigated to evaluate the fuel cell behavior at low ambient temperatures and to derive information on how to properly operate and start up fuel cells in said temperature region.

2 Experimental

2.1 RDE Measurements

All RDE experiments were run 3 times. For each experiment new electrodes were made via ink deposition [15]. A Pt-ring/glassy carbon disc-electrode (Odisc = 5.5 mm, Pine Instruments) was used as substrate for the supported electrocatalyst 60 wt.% Pt/C (HisSPEC9100, Johnson Matthey). The RDE was polished for 15 min to a mirror finish using a trocatalyst 60 wt.% Pt/C (HiSPEC9100, Johnson Matthey). In instruments) was used as substrate for the supported electrocatalyst ink 2 mg of the 60 wt.% Pt/C electrocatalyst was dispersed in a 2 mL 20 vol.% 2-propanol/0.02 wt.% Nafion solution by ultrasonication. The dispersed catalyst ink was pipetted onto the disk and dried for 5 min. The electrode was dried with Ar-gas and then mounted upside down in the electrode rotator. For the catalyst ink 2 mg of the 60 wt.% Pt/C electrocatalyst was dispersed in a 2 mL 20 vol.% 2-propanol/0.02 wt.% Nafion (DE 520, 5 wt.%, EW 1000, DuPont) solution by ultrasonication for 1 h in an ice bath. An aliquot of 12.1 μL of the well-dispersed catalyst ink was pipetted onto the disk and dried at a rotation rate of 700 rpm for 1 h to result in a loading of 30.6 μg cm⁻². All electrochemical measurements were carried out in a standard three-electrode cell with a cooling jacket. A thermostat (Minisstat125, Huber) filled with a 20 wt.% glycol/water mixture was used to control the cell temperature. 0.1M HClO4 (Merck, 70 wt.% Suprapur®) was prepared by diluting with ultrapure water (0.055 μS cm⁻¹) and used as electrolyte. A platinum Pt-plate was used as counter-electrode and a reversible hydrogen electrode (RHE) as reference electrode. All electrodes were connected to a potentiostat (BioLogic Model SP 300). Before the electrochemical measurements the electrolyte solution was purged with Ar-gas for 30 min.

The ORR measurements started by conditioning the electrode by cycling between 0.05 and 1 V vs. RHE at 100 mV s⁻¹ for 50 cycles in Ar-gas saturated electrolyte. The electrochemical surface area (ECSA) was determined by the hydrogen underpotential deposition (Hupd) method. Therefore, cyclic voltammetry (CV) measurements were carried out between 0.05 V and 1 V vs. RHE for 3 times at 20 mV s⁻¹. The ECSA was calculated by integrating the hydrogen deposition area after double-layer correction, assuming a value of 210 μC cm⁻² for the adsorption of a hydrogen monolayer on Pt. For the ORR measurements the electrolyte solution was saturated with oxygen by purging with O₂ for at least 30 min. A typical polarization program (1 V vs. RHE → 0.2 V vs. RHE → 1 V vs. RHE) was carried out at rotation rates of 100, 400, 900, 1,600 and 2,500 rpm at 5 mV s⁻¹. The background current was measured in oxygen-free solution by CV measurement between 1 and 0.2 V vs. RHE at 5 mV s⁻¹. Furthermore, EIS was carried out in order to obtain the electrolyte resistance (R₀) within a frequency range of 100 kHz to 100 mHz at 0.4 V vs. RHE with an amplitude of 10 mV. The ORR current was then corrected by the background current and the electrolyte resistance. Kinetic currents I⁺ were calculated from the anodic sweep (0.2 vs. RHE → 1 V vs. RHE) by the method of Levich-Koutecky as follows:

\[ I^{-1} = I_{L}^{-1} + I_{k}^{-1} \]  \hspace{1cm} (1)

where I₁ is the mass transport limited current.

For studying the carbon corrosion, the electrode was prepared and conditioned according to the same procedure as described for the ORR measurements. Assessment of carbon corrosion consisted of cycling the electrode for 20,000 cycles between 1 and 1.5 V vs. RHE at 500 mV s⁻¹ according to the FCCJ degradation protocol [16] in Ar-gas purged electrolyte solution. Every 1,000 cycles the ECSA was determined as described before. Additionally, at the beginning of life (BOL) and after each C-degradation experiment the ECSA and the ORR activity were measured. The measurement of the ORR experiments differs from that described above that only at one rotation rate of 1,600 rpm the polarization program was carried out. CO stripping voltammetry was also carried out at the beginning of life (BOL) and after 20,000 cycles. The electrochemical cell was purged for 10 min with CO at a rotation rate of 400 rpm, while the RDE was held at 0.05 V vs. RHE. Then the electrolyte was purged with Ar-gas for 20 min removing CO from the electrolyte. Afterwards the potential was swept three times between 0.05 and 1 V vs. RHE at 10 mV s⁻¹. For comparability reasons all CO stripping experiments were conducted at 20°C, since CO stripping voltammetry is strongly affected by temperature.

2.2 Single Cell Tests

5 × 5 cm² membrane electrode assemblies (MEAs) were fabricated by spray coating a Nafion 211 membrane (25.4 μm thickness, Chemours) to form a catalyst coated membrane.
(CCM). For that purpose a catalyst slurry was prepared with a commercial 60 wt.% Pt/C catalyst (HiSPEC9100, Johnson Matthey), a Nafion solution as ionomer (DE 520, 5 wt.%, EW 1000, DuPont) and an appropriate amount of 1/2 water/isopropanol mixture (v/v) as vehicle. The mixture was sonicated with a sonifier (SFX-250, Branson) to form a homogeneous dispersion. The catalyst slurry was then applied by hot-spraying to the Nafion 211 membrane, which was mounted to a stainless-steel plate and heated up to approximately 90°C to vaporize unnecessary solution. The CCMs were then dried at 130°C for 30 min. In such way CCMs were prepared with 30 wt.% Nafion and Pt loadings of 0.4 mg cm⁻² and 0.3 mg cm⁻² for the cathode and the anode, respectively. The CCMs were then sandwiched between two gas diffusion layers (H23C2, Freudenberg) to form a membrane electrode assembly (MEA) and applied to a cell mounting system (qCf25, balticFuelCells GmbH) for testing.

The fuel cell testing was carried out in a climate chamber (C-70/1000, CTS GmbH) to control the ambient temperature. Thermocouples (CO3-K, Omega) inside the cell and the climate chamber were installed to record cell and ambient temperature throughout all experiments. Pure H₂ as anode reactant and air as cathode reactant were used. Reaction gases were supplied humidified at ambient pressures (C-70/1000, CTS GmbH) to control the ambient temperature. Two different Tafel regions, the low current density (lcd) range and the high current density (hcd) range, can be observed due to the oxidation of the Pt catalyst (thermodynamic potential 0.88 V vs. RHE), which is in agreement with the literature [19, 20]. The found Arrhenius apparent activation energy for the lcd range (0.95 V vs. RHE) is 24.5 kJ mol⁻¹, which is in agreement with the work of Paulus et. al, who derived an Arrhenius apparent activation energy of 21 kJ mol⁻¹ in temperature range 20–60°C also in 0.1M HClO₄ at a potential of 0.93 V [21]. We derived an activation energy of 44.8 kJ mol⁻¹ for the hcd region, using the model by Markiewicz et al. [18] obtaining comparable values in the temperature range of 7–60°C (40 kJ mol⁻¹). Derived activation energies in the lcd range and the hcd range are therefore also in agreement with the literature for elevated temperatures. Hence, no change of the ORR mechanism in the investigated temperature range is found. Tafel slopes h_lcd in the lcd range increase with decreasing temperature due to temperature dependence of the charge transfer coefficient α. We derived a slope for the temperature dependence of 1.4×10⁻³ ± 4×10⁻⁴ T, where T indicates the absolute temperature in K. This result agrees well with published values between 20°C and 250°C (1.678×10⁻³ T) [22].

3.2 Carbon Corrosion Measurements

Carbon support corrosion has a major impact on the catalyst degradation and therefore on the durability of the fuel cell. At cathode potentials higher than 1 V vs. RHE, which are typically occurring at start/stop events, carbon atoms can leave the cell as CO or CO₂ (thermodynamic potential 0.21 V vs. RHE for the CO₂ formation). Pt nanoparticles will be detached from the degrading support and removed from the electrode.

In Figure 3 the effect of the catalyst support degradation experiments on the electrochemical surface area (ECSA) is shown. In the investigated temperature range of 0–20°C. Potential cycles were carried out between 1 V and 1.5 V vs. RHE with a scan rate of 500 mV s⁻¹ according to the FCCJ degradation protocol [16]. The ECSA was measured every 1,000 cycles by underpotential hydrogen deposition sweeping the potential between 0.05 V vs. RHE to 1 V vs. RHE three times at a scan rate of 20 mV s⁻¹ [23]. Figure 4 shows representative cyclic voltammograms for the ECSA determination at 20°C after several high potential cycles. With decreasing temperature less ECSA is lost because of reduced carbon degradation or rather concomitant Pt dissolution due to the slower kinetics of the carbon oxidation to CO and CO₂. Moreover,
Pt agglomeration affects the ECSA and is also slowed down at lower temperatures. It can be observed that with increasing cycles less ECSA is lost per cycle.

In general, parameters such as high temperatures (50–90°C), high water content, high oxygen concentrations and a low pH accelerate carbon corrosion on the cathode side [24]. In detail, a number of further effects can have an influence. So beside the carbon corrosion, the reduction of the active platinum surface area by effects such as platinum dissolution or Ostwald ripening has a similar strong contribution to the catalyst degradation. It

Fig. 1 a) Representative uncorrected RDE polarization curves in oxygen saturated 0.1M HClO₄ of a 60 wt.% Pt/C catalyst (HiSPEC9100, Johnson Matthey) at 1,600 rpm for 25°C and 5°C with a loading of 30.6 μg(Pt) cm⁻². b) Background current and iR-drop corrected polarization curves. c) Derived kinetic currents from anodic sweeps (0.2 vs. RHE → 1 V vs. RHE) according to Levich-Koutecky using polarization curves from 100, 400, 900, 1,600, and 2,500 rpm. d) O₂-solubility corrected kinetic currents according to Markiewicz et al. [18].

Fig. 2 Tafel plots of ORR at temperatures 0, 5, 10, 15, 20, and 25°C. Current densities are corrected by the oxygen concentration. Data processing was conducted as shown in Figure 1.

Fig. 3 Effect of carbon degradation measurements on the ECSA.

Pt agglomeration affects the ECSA and is also slowed down at lower temperatures. It can be observed that with increasing cycles less ECSA is lost per cycle.
is often assumed that both effects are separate and can be pro-
voked by separate conditions. So accelerated stress test suite pro-
posed by the fuel cell commercialization conference of Japan 
FCCJ foresees separate tests for potential jumps between 0.6 V 
and 1.0 V. According to Omura et al. [16] this test should emulate 
load cycles during driving, which principally affects only the 
catalyst particle, whereas a second test with triangular fast 
potential cycling between 1.0 V and 1.5 V shall induce carbon 
corrosion. More recent results by Pizzutillo et al. [25] indi-
cated, however, that such a strict separation of both processes is 
not possible, as consecutive execution of both tests will increase 
the degradation along both pathways. One reason is the cataly-
tic activity of platinum for the carbon corrosion, which was 
studied, e.g., by Linse et al. [26]. They found that Pt can enhance 
the carbon corrosion up to potentials of 1.4 V and that this effect 
is enlarged, if the potential is intermittently cycled to lower val-
ues. Thereby, also the lower potential vertex value is of impor-
tance. So the reduction of the lower vertex potential from 0.6 V 
vs. RHE to 0.15 V vs. RHE caused a strong increase of carbon cor-
rrosion, albeit both values are below the platinum oxide reduc-
tion potential. An idea of the cause can be gained from the 
DMEs results obtained by Aston and Arenz, who investigated 
different carbon supports without platinum loading [27, 28]. 
They found that in the high potential region not the entire fara-
daic current can be assigned to the formation of CO2, but that 
the concomitant Pt dissolution. Another possible explanation is 
an initial fast corrosion of amorphous or low graphitized carbon 
support structures, whereas higher graphitic domains corrode 
slower.

Furthermore, preferably small Pt nanoparticles will corrode 
first due to Ostwald ripening. For Ostwald ripening, small Pt 
nanoparticles will dissolve, because of decreased cohesive 
energy and re-deposit on larger particles on the electrode surf-
ace. Also Pt particles merge to bigger particles undergoing 
agglomeration or sintering [29–31]. Thus, an increase of the Pt 
particle size is expected, which leads to a lower amount of active Pt sites for catalytic carbon corrosion. The size increase 
of these Pt particles due to Ostwald ripening and agglomera-
tion on the surface was indirectly investigated by CO strip-
ing voltammetry (Figure 5). Maillard et al. showed that CO 
stripping voltammetry of Pt/GC (glassy carbon) electrodes is 
size sensitive [32]. Single small particles less than 3 nm have a 
high CO oxidation overpotential whereas Pt agglomerates 
have a high catalytic activity towards CO oxidation. As a 
result, Pt agglomerates show a reduced oxidation overpotential 
of ca. 90 mV. Hence, in Figure 5 the high oxidation peaks at 
c. 0.8 V vs. RHE can be correlated to CO oxidation by small 
Pt particles and the pre-peaks at ca. 0.6–0.7 V vs. RHE to Pt 
agglomerates, respectively. With increasing temperature in the 
cycling measurements, the area under the pre-peak increases 
and simultaneously the small Pt particle peak at high overpo-
tentials decreases even stronger. This reveals that with increas-
ing temperature in the investigated temperature range 0–20°C 
the expected Ostwald ripening and agglomeration of small Pt 
particles is accelerated. The rise of the ECSA trends at the start 
of the experiment can be explained by conditioning and clean-
ing of the electrodes.

Before and after the durability experiments of the carbon 
support ORR measurements at the RDE were carried out. The
observed overall ORR activity loss after cycling was very small. Surprisingly, the specific ORR activity \( \text{A m}^{-2} \text{Pt} \) increased in almost all experiments after 20,000 cycles in comparison to the uncycled electrode (Figure 6). The average increase for 20°C was about 20% of the initial specific ORR activity whereas for 0°C just a slight increase of about 1.5% can be observed. In a single experiment at 0°C a decrease of ca. 1% was measured.

An explanation for the increase of the specific ORR activity could be the Ostwald ripening and agglomeration of small single Pt particles, of which some were inactive towards the ORR in the first place. For very small Pt particles < 1.5 nm the specific ORR activity in \( \text{HClO}_4 \) solution decreases rapidly [33]. Following the trend of the curve one can conclude that even smaller single Pt particles are inactive towards the ORR. Moreover, agglomeration of small Pt particles leads to a lower amount of accessible sites for underpotential hydrogen deposition resulting in a decreased ECSA (see Figure 3). If some of the dissolved particles were inactive in terms of ORR, e.g., not accessible for \( \text{(OH)}_{\text{ads}} \) or unable to adsorb \( \text{O}_2 \), the specific ORR activity would increase. Therefore, the increase of the specific ORR activity would be strongly affected by the manufacturing process and surface morphology of the electrode, which would also explain the large error bars in Figure 6.

Another explanation for this phenomenon could be the particle size dependence of the specific ORR activity. The ORR activity is largely affected by the morphology and the shape of Pt particles, e.g., kink and edge sites or other surface defects, which usually have higher catalytic activity [29]. Shao et al. recently showed that the specific ORR activity increases with particle size in the range of 1–5 nm as a result of too strong oxygen binding energies on edge sites of small nanoparticles [33]. The initial size of the HiSPEC9100 is 2.8 nm (max) which is in the middle of the investigated size range of Shao et al. Furthermore, agglomeration pre-peaks in the CO stripping voltammetry occur already for particles bigger than 3 nm (see Figure 5) and therefore can detect size increase in this range [32]. Hence, the change of the morphology of the emerging agglomerates due to Ostwald ripening and agglomeration could possibly increase the specific ORR activity.

### 3.3 Single Cell Tests

For additional insight into catalyst behavior in the temperature range 0–20°C under real operating conditions we tested Pt/C catalyst via single-cell measurements inside a climate chamber. The membrane electrode assembly (MEA) consisted of Nafion 211 membrane, spray coated with Pt/C catalyst (HiSPEC9100, cathode: 0.4 mg cm\(^{-2}\) Pt, anode: 0.3 mg cm\(^{-2}\) Pt) and Freudenberg gas diffusion layers. Gases – \( \text{H}_2 \) and air with a stoichiometry \( \text{l} \) of 2 and 4, respectively – were supplied humidified via bubbler inside the climate chamber, except for the measurement at 0°C, which was run using dry gases. Measurements comprised polarization curves being recorded with intermittent cooling after each measurement point and galvanostatic long-term tests at the corresponding power densities in the range 1/3 \( \text{P}_{\text{max}} \)– \( \text{P}_{\text{max}} \). Power densities were ascertained from polarization curves. Before measurements the cell was activated overnight at 60°C. Results for polarization curves are shown in Figure 7. Figures 8–10 show the cold starts at different loadings for the climate chamber temperatures 20, 10, and 0°C, respectively.

Initial cell performance at 60°C agrees reasonably well with values reported by Bi et al. [34], who reported 0.70 V @ 600 mA cm\(^{-2}\) at 60°C, whereas our cell showed 0.62 V at the same conditions and a lower loading – 0.4 mg cm\(^{-2}\) Pt. As seen in the polarization curves, lower temperatures expectedly resulted in significantly lower performance, including higher activation losses, larger cell resistance and in case of the 0°C measurement also significant mass transport losses. During galvanostatic operation (Figures 8–10) the cell temperature rises due to entropic heat, overpotential of the reactions and ohmic losses through
Even though a rising cell temperature leads to better performance – decelerating cell heating – a constant cell temperature is reached quickly due to limited hydration of the membrane at constant current and heat removal due to a rising temperature gradient between cell and climate chamber. As the cell was not insulated, constant ambient cooling inside the climate chamber leads to strong heat removal. ∆Tcell and heating rates (slope at 50% Tmax) vs. P * P−1max are shown in Figure 11. Rising ambient temperature leads to higher ∆Tcell due to less cooling via gas flow and rising power density results in a higher ∆Tcell due to higher currents. Pmax at 0°C had to be run at double λ, as probably the issue of electrode flooding was impeding cell operation at lower stoichiometry. Consequently, ∆Tcell as well as heating rate do not follow the trend observed for the higher ambient temperatures, since a higher λ equals stronger cooling from ambient temperature gases.

Steady state cell temperatures and heating rates (at 10 and 20°C) increased in a nonlinear fashion with the highest temperature (∆Tcell of 19 and 22 K) and heating rate (0.25 and 0.4 K min−1) being reached at Pmax, indicating that the ohmic and reaction heat has a bigger effect than the corresponding cooling via gas flow. Only at twice the gas flow rates (stoichiometry 4 for H2 and 8 for air, unhumidified) at 0°C and 230 mA cm−2 corresponding to Pmax a significant cooling effect was observable. Heating rates compare well to the 0.46 K min−1 reported by Tabe et al. at 700 mA cm−2 and 45°C cell temperature [36], corresponding to our measurement at 20°C and Pmax. Higher heating rates reported in other cold start experiments can be explained by different experimental setups and operation parameters. Yan et al. reported a heating rate of 2 K min−1 at a similar 25 cm² cell.
cold starting from –5 °C, but used preheated feed gases. Santamaria et al. on the other hand obtained 1 K min⁻¹ at 400 mA cm⁻² and –4 °C to –6 °C (corresponding to our 0.25 K min⁻¹ at 10 °C, \( p_{\text{max}} \)) but used a membrane with twice the thickness [37], resulting in higher ohmic heating. 1.8 K min⁻¹ at 600–900 mA cm⁻² was achieved by Lin et al. at –3 °C to –10 °C [38], however using an insulated cell and starting up in constant voltage mode.

Weng et al. showed that water flooding increases as gases are applied with low stoichiometries and/or low cell temperature. Low stoichiometries lead to slow removal of produced water on the cathode side. Moreover, exponential decrease of water vapor pressure with decreasing temperature reduces water uptake in the air gas stream [39]. While the vapor pressure at 80 °C is 47.4 kPa, it is only 2.3 kPa, 1.2 kPa, and 0.6 kPa at 20, 10, and 0 °C, respectively, [40]. Especially at higher current densities this leads to flooding of the electrode as the generated water cannot be removed efficiently from the cell. This water accumulation leads to catalyst surface being covered and thus unavailable for reaction, as well as blocking of catalyst layer and gas diffusion layer porosity, hindering mass transport. A thin membrane exacerbates the problem as its water uptake is minimal. Therefore, flooding of the cell is most likely being seen in Figure 10, where the cell potential shows high noise with many spikes. These may correspond to liquid water droplets being removed from the electrode with a corresponding increase in cell potential due to a larger catalyst ECSA becoming available. Hence, steadily decreasing cell potential at 0 °C and \( p_{\text{max}} \) may be due to the large amount of water being generated. In this experiment an increase in cell voltage up by approximately 140 mV can be seen at 12 h, which is followed by a cell temperature decrease. Since the cell voltage increase is happening abruptly, a spontaneous change must have happened in the cell, like for example removal of accumulated water in the gas diffusion layer (GDL) or the flow fields. This spontaneous change leads to a slight decrease of the cell temperature in the next hour. An attempt of running the cell at 0 °C and \( p_{\text{max}} \) with stoichiometries of 2 and 4 (anode and cathode, respectively) failed. Even though the cell temperature rises quickly to 8 °C (within 40 minutes), the cell potential varies between 0.2 and 0.4 V and drops below the cut-off value (0.2 V) of the setup at 42 min, shutting off the cell. As mentioned, doubling of the stoichiometries on both sides resulted in a successful cold-start at 0 °C, which is in agreement with Weng et al. observing a maximum cell performance at oxygen stoichiometric flow rate of 6 at 50 °C cell temperature [39].

4 Conclusions

In summary, RDE investigations of the catalyst activity towards ORR show equal behavior to elevated temperatures in terms of activation energy and Tafel slopes. Therefore, no change of the reaction mechanism on Pt near the freezing point is concluded. Furthermore, RDE studies of carbon support degradation show a minor effect striking at low temperatures due to slower kinetics, which leads to a less decrease of the overall ORR activity. In contrast to higher temperatures, no significant increase of the specific ORR activity was seen at 0 °C, which could be explained by the fact that the loss of ECSA outweighs the change of Pt morphology towards more active sites. In the feasibility study on single cell level it was possible to operate and start up the cell at current densities up to 230 mA cm⁻² for 0 °C ambient temperature. High current densities in the startup process lead to high heat release and therefore fast increase of voltage and concomitant cell performance. Although the cell temperature rises quickly to values over ambient temperature, water vapor pressure is still too low to overcome effective water removal, especially at 0 °C. At 0 °C and lower stoichiometries (4 for air and 2 for H₂) a cold start attempt failed. Since doubling the stoichiometries leads to a successful cold start together with the fact of low water vapor pressure and a noisy voltage signal, we suspect flooding as the problem starting up the cell. Performance issues due to decreased catalyst activity at lower temperatures are therefore found to be less striking.

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List of Symbols

\( i_k \) Kinetic current / A
\( j_k \) Kinetic current density / A cm⁻²
\( P \) Power density / W cm⁻²
\( p_{\text{max}} \) Maximum power density / W cm⁻²
\( R_{\text{el}} \) Electrolyte resistance / Ω
\( T_{\text{cell}} \) Cell temperature / °C
\( \lambda \) Stoichiometric factor

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