HyCoRA – Hydrogen Contaminant Risk Assessment
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Deliverable 4.2 Guidance for the second part of WP1 and WP2 work

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Summary

This deliverable describes the progress in HyCoRA WP4 during the first 20 months regarding the specification of a probabilistic risk model for hydrogen fuel quality. The risk model is aimed to capture the knowledge on fuel quality and PEMFCs in automotive applications in the form allowing assessing the risk of fuel quality induced problems in FC powered vehicles and enhance understanding on the right level of fuel quality and required quality assurance (QA) measures.

In the first version of the quantitative risk model, centralised production from natural gas (NG) using the SMR-PSA process is considered as production-purification pathway and carbon monoxide (CO) as single contaminant in the fuel is used in the beginning.

The preliminary results show that even with low loading \(0.05\, \text{gPt/cm}^2\) anode MEAs, the CO level needed is over ppm before any incidents can be recorded. The sensitivity analysis, however, show that in worst scenarios the incidents can start at the level 0.5 ppm. Therefore, more experimental data with low loading anodes is needed for improving the model.

The most critical issue for the further development of the model is the possible increased sensitivity to CO surface coverage, when the catalyst is aging. The other critical issues for the further development of the risk model based on the CO coverage are the effect of \(\text{CO}_2\), the rate of CO oxidation during the drive cycle and the rate of CO oxidation during the stoppage. The last one, is, however highly system dependent and more valuable results may be possible to reach with modelling effort.

Concerning the vehicle population and usage profiles there are also large uncertainties and simplified assumption are currently used. These would be improved to correspond wider spectrum of vehicle pollution and user profiles.

The further development of the model will take into account the effect of \(\text{CO}_2\) and the effect of sulphur poisoning. This is also given as guidance for WP1 work.
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1. Introduction

1.1 Objectives and scope

In HyCoRA WP4, the objective is to establish a risk model for hydrogen fuel quality risk which provides a systematic framework to:

- quantify the risk of hydrogen fuel quality induced problems (and the associated economic impact);
- give information on the right level of fuel quality and required quality assurance (QA) activities;
- explore the influence of different fuel production processes and feedstock on the optimal/required QA;
- identify and explore the influence of uncertainties in current knowledge and provide guidance for the experimental work especially in HyCoRA WP1;
- explore the influence of technology improvements in PEMFCs and FCEVs.

The scope of the work is limited to proton exchange membrane fuel cells (PEMFC) in automotive applications, and automotive grade hydrogen fuel.

1.2 Summary of the 2nd OEM workshop

In the workshop 9.10.2015, the results of both HyCoRA project and results gained by other organisations (NPL, LANL) were presented. OEM feedback was mostly collected by e-mails after the workshop. Concerning the qualitative and quantitative risk model in WP4, there were no objections against the model based on CO coverage level.

2. Modelling of the hydrogen fuel quality risk - Qualitative

2.1 Modelling approach

Hydrogen fuel quality risk comprises of:

- the risk of fuel cell operated vehicles (FCEVs) experiencing significant adverse effects due to quality of the hydrogen fuel used, and
- the likelihood of hydrogen refuelling stations (HRSs) delivering hydrogen fuel of such malign quality.

Fuel quality refers here to small concentrations of contaminants (i.e. impurities) in the hydrogen fuel that, if present, affect adversely on PEM fuel cell performance. International standards, such as ISO 14687-2:2012 giving interim quality specifications for hydrogen fuel delivered at refuelling stations and used in proton exchange membrane (PEM) fuel cell applications on road vehicles (ISO, 2012), have been issued to control the risk.

In order to clarify the risk modelling process and keep it better manageable, a step-wise process for building the risk model gradually has been selected. This implies developing the first risk model versions around a relevant example case with limited scope. Once found
feasible, the model scope can be expanded from there to include the most likely hydrogen fuel production methods and feedstocks, and all important contaminants.

The feedback from the 1st OEM workshop (30.9.2014) was that the risk model should be kept simple. Therefore, the focus of the risk model development was placed on the hydrogen produced by centralised production from natural gas (NG) using the SMR-PSA process. Carbon monoxide (CO) was considered as single contaminant in the fuel most suitable as the starting case for risk modelling.

The NG-SMR-PSA-gas truck delivery path can be considered as one of the most common ones and also the one that contains significant risks for the fuel quality failure. In practice the risk is mostly on CO level and sulphur level and therefore also the fuel quality sensor development is focused on those contaminants.

2.2 Qualitative risk model

Tentative influence diagram (ID) models have been outlined previously in the HyCoRA project for considering the risk of CO contamination in HRS dispensed fuel and the risk of CO induced unacceptable performance impact on FC operated vehicles. These models shown in Figure 1 and Figure 2 have been described in more detail in Deliverable 4.1 and the 3rd periodic activity report. Due to foreseen major challenges in considering the impacts of CO poisoning at the FCEV performance level, modelling of fuel CO impact has been limited, at least initially, to FC stack performance.

![Image](image.png)

Figure 1 Tentative ID model for CO contamination in HRS dispensed fuel

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3. Modelling of the hydrogen fuel quality risk – CO only

3.1 Simulation model for estimating CO concentration variation in NG-SMR-PSA product gas

A coarse initial simulation model has been developed for estimating the variation of CO concentration in the hydrogen gas produced using NG-SMR-PSA process. The developed calculation model combines

- the ANL PSA model simulation data on main process parameters’ impact on PSA product gas CO level; and
- initial probabilistic estimates on the accuracy and errors in the measurement and controlling of these process parameters.

In the calculations performed, the errors in the different parameters were assumed to be independent and follow the same probability distribution. Also, the effects of the different parameters on product gas CO concentration were assumed to be additive.

The developed simulation model has been described in detail previously in the HyCoRA 2nd period activity report submitted on 27.5.2015.

Using this model, initial calculations have been carried out to explore the influence that variation/errors in the PSA process parameters would have on the expected CO concentration in the product gas. In the calculations, errors with respect to the absolute target values of the different parameters were assumed to follow the normal distribution with the mean equal to 0 %, and standard deviation of 0.1, 0.5, 1.0 and 1.5 %.

The results of the initial simulation runs performed indicated insignificant risk of experiencing substandard CO concentrations in the PSA product as long as the standard deviation of the errors in the considered process parameters stay below 0.1 % of the parameter target values. Wider error distributions will create a risk of the CO concentration exceeding the 0.2 ppm limit currently set for automotive hydrogen fuel. With standard deviation of 1.0 %, probability of 0.3 % (i.e. 0.003) was observed for the CO concentration to exceed the 0.2 ppm limit. By increasing the standard deviation of the parameter errors to 1.5 %, the probability of exceeding the 0.2 ppm limit was found to increase little above 1 percent (i.e. 0.012). The results are illustrated in Figure 3.
Considering the effects of variation in the different process parameters separately, the results suggest that product gas CO concentration is most sensitive to variation in the PSA inlet flow rate (PSA-Q) and PSA-operating pressure (PSA-P). Small chance of CO to exceed the 0.2 ppm limit was found if the variation in either of these parameters individually approaches the level of 1.5 % measured as the pdf standard deviation. The 1.5 % standard deviation implies that, with the probability of 0.99, the flow rate would stay within 17.578 ± 0.614 N-m3/min range, and the operating pressure within 18 ± 0.629 atm range. Regarding the other parameters considered, the risk of substandard CO concentration appeared to remain negligible with similar variation present.

Figure 3. Dependence of CO concentration of PSA product gas on the distribution of error in the control of different process parameters. Identical error distributions assumed for all parameters N(0;X%).

Figure 4. The effect of error in the control of different process parameters on CO concentration of PSA product gas. Identical error distribution assumed for all parameters N(0;1,5%).
Obviously, the variation in the individual process parameter values that can be tolerated depends on the CO concentration at which the process is designed to operate normally, and how much it differs from the maximum CO limit specified in the applied fuel quality standard. In the ANL PSA model, the target concentration for PSA output is 0.045 ppm when the process operates at the parameter design values.

If found reasonable, similar models could be applied to cover also the other impurities in the produced hydrogen fuel. Similar to the CO case, the ANL PSA model could be used assess the concentrations of N₂, CO₂, and CH₄, H₂O and sulphur species.
3.2 FC stack impact model – CO only

The modelling is limited to a situation that additional anode overvoltage due to CO poisoning is over 50 mV. When 50 mV is exceeded, the system is stopped. In the literature also 30 mV has been used as stoppage criteria\(^2\).

First version of a simulation model for assessing the risk of ‘FC stack incident’ due to CO in the hydrogen fuel in use has been implemented. The quantitative model considers the impact of CO on the active catalyst surface area on anode taking into account

a) the slow loss of electro-chemically active Pt surface area over time due to particle growth, and

b) the active surface area getting covered by CO during vehicle use in a single day.

If CO coverage of anode active surface area reaches a certain threshold value (40%), critical drop in stack output voltage (50 mV per cell) will occur leading to an ‘incident’. In practice, anode overvoltage is strongly dependent on the current density, in addition to CO coverage\(^3\). In the early stage of poisoning (under 50 mV voltage drop) there will be highly uneven CO surface coverage. Therefore, with 10% average surface coverage in the cell, there can be already 80% surface coverage in the beginning of cell causing significant decrease in local current density.

The estimate for the CO coverage is based on the data gained from HyCoRA project (Deliverable 1.3) as well as literature data\(^4\). This estimate is valid only for low loading anodes (0.05-0.1 mgPt cm\(^{-2}\)). It is also assumed that the threshold value is valid for an aged catalyst with smaller area (due to Pt particle growth).

The simulation model as implemented using the ReliaSoft RENO tool is shown in Figures 5 and 6.

The simulation model considers a vehicle (or FC stack) selected randomly from a vehicle population. The vehicle population is characterized by vehicles’ age (expressed in accumulated running hours) and initial Pt loading (in mg Pt cm\(^{-2}\)).

CO concentration in the fuel in use is another random variable. It is determined by CO concentration in the fuel as delivered by HRSs in refuelling (random variable), fuel level at vehicle refuelling (random variable), and the initial CO level in vessel tank at the time of refuelling.

Selected vehicle and FC stack, with the specified CO concentration in the fuel, is exposed to a drive cycle comprised of sub-cycles with predefined load profiles. Accumulation of CO on the anode catalyst surface during a sub-cycle is calculated and compared to a predefined threshold value representing unacceptable stack performance degradation. If CO coverage exceeding the threshold is encountered, simulation is terminated and a ‘FC stack incident’ is recorded. Otherwise simulation is continued to the next sub-cycle of the drive cycle.


After a completed drive cycle, a stoppage time of random duration is initiated. The stoppage duration is sampled from a distribution of the time between consecutive trips observed for hydrogen operated vehicles in field use (NREL/TP-5600-54860:2012). The reduction of CO coverage on the active anode surface during the stoppage due to oxidation by internal air bleed is calculated.

The stoppage time is added on the time duration of the drive cycle. If the accumulated time does not exceed the time limit set for daily operation, a new drive cycle is started. 16 hours has been assumed as the maximum vehicle daily operating period, and is used as termination criteria for simulation in case an ‘incident’ is not encountered. For the new vehicle drive cycle, CO coverage of the catalyst surface as found at the end of the stop is employed.

CO coverage of the active anode catalyst surface area is assumed to be 0 % at the start of the simulation, corresponding to the FC stack being stopped for over 4 hours, i.e. overnight, before the start. Also, the count of the daily operating time is set equal to zero at the start of the simulation.

Once a suitably large number of simulation runs have been carried out, the probability/risk of experiencing a CO induced FC stack incident in vehicle daily operation can be determined as the ratio of the count of incidents recorded over the simulation runs and the overall number of simulation runs performed.

Figure 5. Flowchart model for FC stack CO impact simulation

Deliverable 4.2
HyCoRA, 7FP FCH JU project no. 621223
Figure 6. FC stack CO impact model implementation in ReliaSoft RENO tool
3.3 Initial available area for CO adsorption and Pt oxidation

3.3.1 Initial platinum loading and area

Distribution of initial platinum loading in the vehicle population is given as input for the simulation model. Currently, typical loading is 0.1 or 0.05 mgPt cm\(^{-2}\). Because of the trend of reducing Pt loading in the automotive FCs, the age distributions can be expected to differ for FC stacks with different initial Pt loading level.

From the work of Hashimasa\(^5\) CO adsorption capacity for the Pt anode can be calculated and it is about 1.24 mmol(CO)/gPt. When this value is used, then at maximum current density (i.e. 1 A cm\(^{-2}\)), 1 ppm CO in fuel increases surface coverage by 0.5%/min, if Pt loading is 0.05 mgPt cm\(^{-2}\).

3.3.2 Anode active area as a function of operating time

One of the main barriers to sustainable long-term operation is degradation of the catalyst\(^6,7\). In other words, the initial surface area of the electrocatalyst reduces with time. Electrochemically active surface area is inescapably lost in two ways: accumulation of potential contaminants such as sulphur and particle growth or dissolution of the catalyst. In this report, the latter is briefly addressed.

According to TEM analyses, the catalyst particle growth takes place via two different mechanisms\(^8\). In the nanometer-scale Ostwald ripening, smaller Pt particles dissolve in the ionomer phase forming Pt\(^{2+}\) and then redeposit on larger neighbouring Pt particles. In micrometer-scale, Pt\(^{2+}\) ions diffuse toward the cathode/membrane interface where crossover hydrogen from the anode reduces platinum ions to solid Pt precipitate.

There are plenty of studies concerning the degradation of the cathode catalyst\(^9,10\) but only a few decent articles concentrate also on the anode. When comparing anode and cathode degradation, TEM and XRD analyses reveal that the cathode catalyst particles agglomerate more rapidly\(^11,12\). Clusters formed at the cathode are 1–3 nm larger in diameter, thus


resulting in lower surface area. The difference has been attributed to several plausible factors such as higher dissolution potential of Pt at the cathode, local heat produced by the oxygen reduction, and higher hydration level facilitating the particle growth at the cathode.

Wilson et al. have reported that the Pt surface area reduces to about 65% of the initial area on the anode after 4000 h of continuous operation. From their study, it can be approximated that after 1000 h the area is still close to 80% of the initial value. This is in good agreement with study of Mathias et al.\(^{13}\). On this basis, it could be argued that the PEMFC anode may lose at most 35% of its Pt surface area due to degradation only within first 4000 hours.

In the ‘CO only’ model anode active Pt surface reduction due to this particle growth over FC operating time is taken into account. Active surface area reduction due to irreversible (Cl-) or almost irreversible (S-species) contamination is not taken into account.

As first approximation used in the current simulation model, active Pt surface area reduction is assumed to be linear over time, so that the active area is halved from the initial in 5000 hrs of operation. This implies Pt area degradation rate of 0.01% per operating hour.

The active Pt area at the start of the simulation is calculated as:

\[
\text{StartArea} = \text{InitialArea} - (\text{StackAge (hr)} \times \text{Pt DegradationSpeed} \times \text{InitialArea/100})
\]

### 3.4 Drive cycle

Fuel Cells Dynamic Load Cycle (FC-DLC) is used as first approximation for FCEV drive cycle. The test cycle has total duration of 1181 sec and is defined by 35 Test Points (TP) as shown in Figure 7. The specific loads and durations of the different TPs are described in Table 1. The 100% TP is defined by the electrical load (current density) at 0.65 V. The average load level calculated over the FC-DLC cycle is 28.14%.

![Figure 7. The Fuel Cells dynamic Load Cycle (FC-DLC)](image-url)

FC-DLC is based on the New European Driving Cycle (NEDC) designed for assessing the emission levels of car engines and fuel economy in petrol-based passenger cars. It is supposed to represent the typical usage of a car in Europe. It consists of four repeated ECE-15 urban driving cycles (UDC) and one Extra-Urban driving cycle (EUDC) as shown in Figure 7. The urban driving cycle (UDC) has been designed to represent typical driving conditions of busy cities, while the Extra-Urban Driving Cycle (EUDC) represents high speed driving modes.

The 100% (full load) TP is defined by the electrical load (current density) at 0.65 V. This is the main pitfall of the simulation. According to German Association of the Automotive Industry (VDA), the average power in NEDC is only 4 kW, while the maximum power is 34 kW\textsuperscript{14}. In the simulations in this report, however, it is assumed that the step 34 is a full power TP (with 1 Acm\textsuperscript{-2}).

When power level needed in NEDC is compared to the stack power of current FCEVs, it can be seen that there is significant power surplus of actual FC stack is in all current FCEVs.

This means that in the simulations of this report the fuel cell system is more like a hypothetic system for a range extender vehicle than for FCEV (Hyundai ix35 FCEV or Toyota Mirai).

A more accurate drive cycle for the risk assessment should be generated from the actual vehicle data collected by NREL or other institute. Alternatively, a large number of real or synthetic user days could be run through the model. The data for forming these user days should be collected from FCH JU or other large FCEV demonstration projects so that user data is representative for the future user of FCEV. Alternatively, ICE vehicle data could be used, as it could be assumed that FCEV user profiles are not far from ICE user profiles.

3.5 CO oxidation during the drive cycle

CO on the surface is continuously oxidised by the oxygen coming through the membrane. The phenomena is called as internal air bleed. In practice, the CO oxidation speed due to internal air bleed is dependent on large number of parameters (membrane permeability, CO surface coverage, temperature, pressure, humidity, etc.) and very difficult to estimate. There is no quantitative literature data excluding the single work of Hashimasa et al. (2010). The initial estimate is between 0.03%/min and 0.1%/min of the accumulated CO on the surface. This estimate is valid only for the low loading anode (0.05 mgPtcm$^{-2}$).

Constant catalyst surface CO oxidation speed of 0.1% per minute has been initially assumed in the simulation model to apply when FC stack operates under a load. It is plausible that the CO oxidation speed is a strong function of CO surface coverage. Therefore, using a single value is approximation, which may be modified when better data is available.

3.6 CO coverage calculation during the drive cycle

The amount of CO poisoning of the active surface (in %) occurring during a sub-cycle step depends on CO adsorption speed and CO oxidation speed under load, and the duration of the sub-cycle step.

CO adsorption speed depends on the active catalyst surface area available (% of new MEA), fuel CO level (ppm), and the power level applied (% of stack max).

As an initial estimate for a new MEA with 0.05 mgPtcm$^{-2}$ Pt loading, 1 ppm CO concentration is expected to increase CO coverage by 0.5 % per minute when FC stack is operated at maximum power (1 Acm$^{-2}$). This CO adsorption speed is assumed to reduce linearly as the operating power level, or the fuel CO concentration is reduced. It is increased linearly if electrically active surface area at start is recuced. A simplifying assumption is made here that system efficiency is constant, i.e. the current follows the power one-to-one.

In this case, the increase in CO coverage (%) generated during a drive sub-cycle can be calculated as the sum of CO coverage increase produced in the different sub-cycle steps. As the CO concentration in fuel and the active surface area at start are not considered to vary within the simulation / drive cycles, this can be written as:

$$\Delta CO \text{ coverage (\%)} = \sum_{steps} \left( \text{StepLoad(\%)} \times \left( \frac{CO \text{ Level}}{CO \text{ Ref}} \times \frac{Surface \text{ Area}_{Ref}}{Surface \text{ Area}_{Start}} \times CO \text{ Ads.} \text{ Speed}_{Ref} \right) - CO \text{ Oxid.} \text{ Speed}_{running} \right) \times \text{StepDuration(min)}$$

CO coverage at the end of a drive sub-cycle can then be calculated as the sum of CO coverage at the beginning of the sub-cycle and the CO coverage increase generated during the sub-cycle.
40% average CO coverage of the anode catalyst surface has been assumed initially in the simulation model as the threshold for critical drop in stack output voltage leading to a ‘fuel CO induced FC stack incident’.

3.7 CO clean-up during a start and stop

CO is continuously removed from anode surface due to oxygen permeating the membrane, i.e. the internal air bleed. During a stop of the system, hydrogen concentration around the anode catalyst surface is reduced causing selectivity of oxygen passing through the membrane to increase in oxidising CO vs hydrogen oxidation on the catalyst surface.

As first approximation used in the current simulation model, CO oxidation speed of 0.1 % per minute is assumed for the first hour of stoppage. CO oxidation speed of 0.2% per minute is assumed for the following hours of stoppage. This implies that average CO coverage close to the initially presumed ‘incident’ threshold value of 40% accumulated during driving would get fully removed in 4 hours of stoppage between trips.

It is assumed that the effect of start and stop is not changing, when the system is aging. In practice, the increased permeability of the aged membrane should make the effective S/S time for CO clean-up shorter as the gas exchange time is reduced.

3.8 Start and stop profile

Based on data from 183 vehicles and comprising over 500,000 individual vehicle trips, NREL/TP-5600-54860:2012 has recorded variation in Stoppage time between trips (i.e. On/Off profile) as shown in Figure 8.

<table>
<thead>
<tr>
<th>Stop duration</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10 min</td>
<td>32</td>
</tr>
<tr>
<td>10-20 min</td>
<td>10.5</td>
</tr>
<tr>
<td>20-30 min</td>
<td>5.5</td>
</tr>
<tr>
<td>30-40 min</td>
<td>4.5</td>
</tr>
<tr>
<td>40-50 min</td>
<td>3</td>
</tr>
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<td>50-60 min</td>
<td>2.5</td>
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<td>0-1 hr</td>
<td>58</td>
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<tr>
<td>1-6 hr</td>
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<td>6-12 hr</td>
<td>5</td>
</tr>
<tr>
<td>12-18 hr</td>
<td>5.5</td>
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<tr>
<td>18-24 hr</td>
<td>5.5</td>
</tr>
<tr>
<td>&gt; 24 hr</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 8. Variation in stoppage time between trips

According to Figure 8, 58% of stops are shorter than 1 hour. These 0-1 hour stops follow two-parameter Exponential distribution Exp(14.1;1).

Of the > 1 hour stops about 36% are shorter than 4 hours. In lack of more detailed data, duration of the 1-4 hour stops can be assumed to follow uniform distribution Uniform(61; 240).

For > 4 hour stops the duration can be set to 240 minutes (constant). With the assumed CO clean-up rates for stops, this time is enough to reduce CO coverage on the surface back to zero in all cases that passed the drive cycle without an ‘incident’.
4. CO only model results and sensitivity analysis

4.1 Simulation results

The first version of the ‘CO only’ model has been applied to explore the impact of fuel CO content and FC stack age on the (conditional) probability of FC stack performance loss, i.e. stack incident.

Simulations were performed at three fixed stack ages (0, 2500 and 5000 operating hrs) and fixed fuel CO levels ranging from 0.2 to 4.5 ppm. 0.05 g$_{\text{Pt}}$ cm$^{-2}$ was used as the value of initial anode Pt loading. Three separate simulation runs with 1000 simulations each were performed at each setting. No single incident observed in a simulation run would thus allow considering the probability of incident being less than 0.1%.

In the simulations the FC-DCL drive cycle was applied, in which the stack is operated a short time at full power (i.e. 100% load) during the ‘rural’ subcycle. A stop of random duration sampled from the stoppage time distribution shown in Figure 8 was applied after each completed full drive cycle. Zero CO coverage was assumed at start of the simulation representing a vehicle being stopped overnight. Average CO coverage being more than 40% of the active anode catalyst surface available was applied as the criterion for ‘incident’. 16 hours was assumed as the maximum vehicle daily operating period, and was used as stop criteria for simulations without an incident.

The results of the simulations are shown in Figure 9. The results indicate decreasing tolerance of FC stacks for CO in the fuel according to the age of the stacks; old used stacks being much less tolerant than the unused ones. However, even the old stacks with 5000 operating hours were found to tolerate 1 ppm CO in the fuel without showing noticeable risk for ‘incident’. This is much higher CO concentration than the 0.2 ppm limit currently set in the ISO quality standard for hydrogen fuel in automotive use.

![Figure 9. Conditional probability of experiencing CO induced incident in daily operation of FC stack/vehicles of different ages forecasted with the ‘CO only’ simulation model (0.05 g$_{\text{Pt}}$ cm$^{-2}$ initial loading, FC-DCL drive cycle with stops of random duration in between, average CO coverage > 40% used as criterion for CO incident)]
4.2 Sensitivity analysis

Sensitivity analysis has been performed to evaluate the effects of changes in the simulation model parameters on the forecasted probability of CO induced ‘FC stack incidents’. Model parameters related to FC stack characteristic have been considered in the analysis. The objective of the analysis has been to identify those parameters in which uncertainty regarding the parameter value would have highest impact on the model results. Future studies could then be directed to those parameters to reduce the related uncertainty and improve credibility of the simulations.

In addition, parameters related to usage of the FC stacks and vehicles would affect significantly the predicted risk of ‘FC stack incidents’. These comprise the drive cycle power profile, the Start/Stop profile, and the age profile of FC stacks/vehicles. Obviously, the simulations will give more credible results the better these profiles capture the actual variation on these parameters in the FC vehicle population.

The sensitivity analyses performed with respect to specific model parameters are described in the following chapters. In the analyses the values for the other model parameters than the one(s) studied were kept at their initially specified value, and the drive cycle and S/S profile as specified in Ch. 3.4 and Ch. 3.8 were applied.

Three separate simulation runs with 1000 simulations each were performed at each parameter setting. Sensitivity of model parameters have been studied here with respect to stacks

4.2.1 CO oxidation rate during drive cycle

The effect of CO oxidation rate by internal air bleed during driving to CO incident risk in daily operation was studied by considering oxidation rate reduction to 0.05 %/min and 0.025 %/min from the initially assumed value of 0.1 %/min.

Reduced oxidation rate during driving was found to increase the ‘CO incident’ probability as shown in Figures X7 and X8. However, as shown in Figures X7 and X8, even with the reduced oxidation rate during driving, even the old stacks with 5000 operating hrs appeared to still tolerate 1 ppm CO in the fuel without showing noticeable risk for ‘incidents’.

The considered reductions in CO oxidation rate during S/S appeared to have slightly stronger impact on model predictions compared to the considered reductions in CO oxidation during driving.

4.2.2 CO oxidation rate during S/S

Following estimates for CO oxidation rate during stoppage were investigated:

- Oxidation rate = 0 during the first hour and 0.25 %/min after that
- Oxidation rate = 0 during the first two hours and 0.4 %/min after that
- Oxidation rate 0.1%/min for the first hour and 0.2%/min after that (assumed initially)

The forecasted risk of CO induced incident was found to be sensitive for the oxidation rate affecting during first two hours of stoppage. The forecasted probability of incident was found to increase substantially when zero oxidation rate was assumed for the first hour or the first two hours of stoppages as specified above. The higher than initially assumed oxidation rates during the following hours would not compensate the lack of oxidation in the beginning of stops.
However, as shown in Figures 10 and 11, even with the reduced oxidation rate during S/S, even the old stacks with 5000 operating hrs appeared to still tolerate 1 ppm CO in the fuel without showing noticeable risk for ‘incidents’.

The result shown here is obviously affected by the stoppage time distribution assumed for FC stacks/vehicles claiming about 60% of stops lasting less than an hour and 65% of stops being shorter than two hours.

In other words, the time needed for starting the CO oxidation during the stoppage has high importance. It is, however, difficult to study experimentally as the exact design and operation of the automotive system is not known.
4.2.3 Increased sensitivity with aged catalyst

It was initially assumed that the sensitivity of the anode Pt surface to CO coverage is not changing when the FC stack gets older. Consequently, 40% average CO coverage of the anode catalyst surface was assumed initially in the simulation model as the constant threshold for a ‘fuel CO induced FC stack incident’

The sensitivity to this assumption has been tested by considering having the threshold CO coverage level reducing from the initial 40% for a new FC stack to 30% by 2500 hours of operation and further to 20% by 5000 hours.

As shown in Figure 12, the simulation model is strongly sensitive to this model parameter value. Obviously, if surface sensitivity is not constant but the surface becomes more (or less) vulnerable over the accumulated operating hours, the impact (i.e. error) on model predictions gets larger over time.
4.2.4 Combinations of worst case situations

As a worst case scenario, the combined effect of low oxidation rate during the drive cycle, low oxidation rate during S/S, and increased sensitivity to CO coverage on the anode Pt surface, as the FC stack gets older were considered. The combined effect consisted:

- 0.025 %/min CO oxidation rate during driving,
- zero CO oxidation rate during the first two hours of stoppage, and 0.4 %/min after that,
- 20% average CO coverage and 30% average CO coverage as the criterion for ‘CO induced incident’ for FC stacks having operated for 5000 hours and 2500 hours, respectively.

As shown in Figure 13, such changes in the model parameters would lead to strong shift of the forecasted incident probability curves to lower CO concentrations in fuel.
Figure 13. Combined effect of reduced CO oxidation rate in driving and S/S and increased Pt surface sensitivity to CO coverage over FC stack age on ‘CO only’ simulation model forecasts on CO induced incidents.
5. Extension of the CO based risk model

The further development of the CO based model should take into account the combined effect of especially CO and CO\(_2\). In addition, some other impurities (e.g. formic acid and formaldehyde) can also form CO on the surface. In addition, the slowly reversible loss of surface area due to sulphur contamination should be taken into account.

The carbon dioxide limit of the ISO 14687-2:2012 and ISO 14687-3:2013 (category 3) is 2 ppm. Therefore, the reasonable maximum level for CO\(_2\) would be 1000 ppm assuming 99.8% fuel utilisation rate for the FC system.

However, even in the absence CO\(_2\) in the hydrogen fuel, there will be some CO\(_2\) in the anode gas as there will be permeation to the anode, especially in wet conditions (Ma, Odgaard and Skou, 2005). Therefore, there will always be some CO\(_2\) on the anode even if the hydrogen fuel is completely CO\(_2\)-free. In the measurements of HyCoRA project several hundred ppm could be measured in the anode recirculation loop, even if hydrogen 6.0 was used (3\(^\text{rd}\) periodic report / Deliverable 6.4).

The unavoidable existence of CO\(_2\) on the anode side means that there can always be formation of CO via a reverse water gas shift (RWGS) reaction or via electrochemical reaction (Kortsdottir, Fernandez and Lindström, 2013)\(^{15}\).

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & \leftrightarrow \text{CO} + \text{H}_2\text{O} & \text{RWGS} \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- + \text{Pt} & \leftrightarrow \text{Pt} - \text{CO} + \text{H}_2\text{O} & \text{Electrochemical reaction}
\end{align*}
\]

The effect of CO\(_2\) and the importance of CO formation via RWGS have been discussed in a number of studies, most of which are reviewed by Du, Pollard, Elter and Ramani, (2009).

Kortsdottir, Fernandez and Lindström (2013) have recently published a highly interesting study in which they show that CO coverage ratios of 50% or more can be achieved on the platinum surface, when there is 20% CO\(_2\) in the anode gas (N\(_2\) or H\(_2\)).

However, the effect of CO\(_2\) has not been studied experimentally in the levels relevant to ISO 14687-2:2012 and not in combination with sub-ppm level of CO. In principle, if there is a formation of CO on the platinum surface via RWGS or electrochemical reaction, this should be observed as lower CO tolerance and shorter poisoning time.

According to modelling work of Ahluwalia and Wang (2008), the acceptable level of CO\(_2\) would be two orders of magnitude higher than the limit in ISO 14687-2:2012. However, there is not enough experimental evidence for revising the limit of CO\(_2\).

According to the data from Kortsdottir, Fernandez and Lindström (2013) the formation of CO on the Pt surface via electrochemical reaction is a relatively rapid process and takes place within few minutes. On the other hand, anode gas volume in automotive fuel cell system is in the range of 0.1 dm\(^3\)/kW\(_\text{peak}\) (Ahluwalia\(^{16}\)). It will, therefore, take from few minutes to few tens of minutes to reach steady-state CO\(_2\) concentration in the anode gas.

Based on above, it can be concluded that there is some transient time to reach steady state CO\(_2\) concentration in the anode gas and CO coverage on the Pt surface. However, for keeping the model simple, steady state CO\(_2\) concentration in the anode gas and...
corresponding CO coverage on the Pt surface and will be assumed. CO coverage dependency on CO$_2$ concentration and temperature is currently not known and could be included in the model only for illustrative purpose.

In the earlier work to model the effect of contaminants, both formic acid and formaldehyde have been considered to form CO on the catalyst surface by dissociative adsorption.$^{17}$ However, the results of WP1 and WP3 indicate that the effect of formic acid and formaldehyde can be much weaker than the effect of CO. In addition, it seems unlikely that formic acid and formaldehyde would be exceeding their low limits in ISO 14687-2:2012. Therefore, at this stage, the risk model will be further developed to take into account only CO$_2$, and excluding formic acid and formaldehyde.

When the risk model is further developed, more data for the loss of CO adsorption capacity due to sulphur contamination is needed. In addition, the critical surface coverage for CO should be studied, when active area is reduced. This requires experimental data with MEAs with lower Pt loading than 0.05 mg/cm$^2$.

6. Guidance for the second part of WP1 and WP2 work

The results of the risk analysis and additional information published in the literature are valuable for the further guidance of the work especially in WP1 but also in WP2 and WP3.

In WP1 the work should be continued with low loading anodes (0.05 mgPt/cm$^2$ or less). The maximum and average current levels should be similar, when FC-DLC is applied as the molar flow rate of the contaminant will depend on the current density used.

In the risk based hydrogen quality assurance, the importance of formic acid and formaldehyde is reduced as these are not present in the main production paths. Further work with these contaminants is, however, relevant as the limits may be changed.

For formic acid and formaldehyde there is an assumption of build-up of contaminants$^{18,19}$ behind the limits in ISO 14687-2:2012. In practice, permeation to the cathode, dissolution in the water and oxidation to CO$_2$ will limit the accumulation of the contaminants. However, this must be verified. Measuring these mitigating phenomena or measuring the contaminant accumulation is very difficult, especially for formic acid. Due to this, for possible revision of formic acid and formaldehyde limits in ISO 14687:2-2012, measurements with HCOOH/HCHO in hydrogen are needed to reach fuel utilisation of higher than close to 99.8%, which seems to be possible to reach only with system level measurements.

As shown in the Deliverable 1.3, the effect of start-up and shut-down is clearly measurable. However, it will depend on the stack and system design, used components and operation (gas volumes, gas compositions). In addition, the membrane permeability has importance as it determines the time scale for gas exchange between the anode and cathode. Therefore, for improving the accuracy of model, the data should also be gained with modelling efforts.

In WP2 and WP3 the work could be focused more risks associated with different production-purification-delivery paths, as described in TIR J2719/1$^{20}$.

$^{18}$ http://www.hydrogen.energy.gov/pdfs/review10/fc017_ahluwalia_2010_o_web.pdf
$^{19}$ https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/fp_workshop_watanabe.pdf, slides 24-25