

Effect of Toluene on PEMFC Performance[▲]

J. Viitakangas^{1*}, S. Auvinen¹, M. Costantino², S. Viik¹, J. Ihonen¹

¹ VTT Technical Research Centre of Finland Ltd, Tietotie 4 C, Espoo, P.O. Box 1000, FI-02044 VTT, Finland

² Politecnico di Torino, Department of Energy, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy

Received May 21, 2019; accepted January 13, 2020; published online May 18, 2020

Abstract

Liquid organic hydrogen carriers (LOHCs) are promising means for hydrogen transportation. They are compatible with existing liquid fuel transport infrastructure and enable for efficient and safe hydrogen storage and transfer over long distances. Toluene and dibenzyltoluene are considered the two most promising LOHCs. Toluene is probably a contaminant found in hydrogen released from these LOHC liquids.

The impact of hydrocarbon contaminants on automotive type fuel cells has been analyzed to a limited extent, and a few species only have specific limits (CO, CO₂, HCOOH, HCHO, CH₄). Currently, hydrocarbons are limited to a total of 2 ppm (methane basis) in the automotive hydrogen fuel standard,

ISO 14687:2019. This may lead to strict impurity levels for species from LOHC, and therefore higher costs of hydrogen purification and quality assurance.

This work presents contamination studies with toluene. The measurements were conducted using a PEMFC short stack with anode recirculation and with high fuel utilization (98%). The results show no effect or only a small contamination effect with up to 20 ppm toluene, and clear contamination with 50 ppm toluene. This supports the need for more studies so that a separate limit can be defined for toluene in future versions of the ISO 14687.

Keywords: Fuel Cell, Hydrogen, Hydrogen Fuel Impurities, Liquid Organic Hydrogen Carriers, PEMFC, Toluene

1 Introduction

Decarbonization of transportation requires serious efforts in the near future. Hydrogen fueled vehicles with polymer electrolyte membrane fuel cell (PEMFC) stacks offer a great solution for variable transport needs. For a feasible hydrogen economy, hydrogen fuels need to be safe, available and affordable. Liquid organic hydrogen carriers (LOHC) are one choice for the safe transportation of hydrogen, and LOHCs are compatible with the existing liquid fuel transportation infrastructure. LOHCs are commonly non-hazardous, non-toxic liquids, which are also safe to store, because no high pressures or temperatures are required. There are a wide variety of different LOHCs suitable for hydrogen storage for transportation [1], toluene and dibenzyltoluene being two promising ones, and they are being commercialized in Germany and Japan. However, every delivery path of hydrogen transport to the refueling station may cause small amounts of impurities to hydrogen fuel. Impurities possibly deriving from toluene and dibenzyltoluene are similar, because the decomposition products of dibenzyltoluene have been detected to be mainly

methane, toluene, benzene, methyl cyclohexane and cyclohexane [2].

In addition, even small quantities of water dissolved in the LOHC have been demonstrated to react to CO and CO₂ under catalytic dehydrogenation [3].

Toluene is one of the most common potential impurity, when toluene or dibenzyltoluene is used as a hydrogen carrier. There are only a few studies about toluene as a hydrogen impurity. Dorn et al. [4] measured a small overpotential of 2 and 8 mV with 2 and 20 ppm toluene, respectively, in fuel cell operation. Bender et al. [5] detected no significant cell performance change with 20 or 60 ppm toluene. Similarly, no substantial fuel cell degradation with 20 ppm toluene was reported by Wang et al. [6]. Kortsdottir et al. [7] observed an increase in charge transfer resistance with 2,000 ppm of toluene in a symmetrical H₂/H₂ cell, while 120 ppm did not have an effect. They also introduced 170 ppm toluene to a fuel cell under constant load operation and saw no loss in cell potential.

[*] Corresponding author, jaana.viitakangas@vtt.fi

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

[▲] Paper presented at the 8th International Conference on Fundamentals and Development of Fuel Cells (FDFC2019), held 12–14.02.2019 in Nantes, France.

In practical applications, the impurities can be present as mixtures. Unfortunately, only a limited number of studies has been performed, and the combined effects of different impurities are still not well known. Dorn et al. [4] observed an impurity mixture of 2 ppm CO and 20 ppm toluene cause a greater overpotential than the sum of the overpotentials of the single impurities. However, their platinum loading at the anode was high, $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. Angelo et al. [8] studied the mixture of CO and toluene with MEAs with the anode platinum loading of $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. They observed no additional effect on PEMFC performance with the mixture of 2 ppm toluene and 0.2 ppm CO compared with contamination with 0.2 ppm CO solely.

In addition, the contamination dynamics may be different with contaminant mixtures compared with single contaminants. Shi et al. [9] noticed that the effect of 50 ppm CO and 10 or 20 ppm H₂S mixtures has different behavior in the beginning and further phase of poisoning, when compared with the summation effect of two impurities alone. The effect of the impurity mixture was more detrimental in the initial phase of the poisoning as the calculated effect. However, in the later phase, the mixture's effect was less severe than the calculated summation effect of two impurities alone, due to the high concentration of CO that inhibited the adsorption of H₂S and therefore, decreased the H₂S coverage compared with the situation with H₂S as a sole impurity.

All of the above studies were conducted with PEMFC single cells in test systems, which are rather dissimilar to the automotive PEMFC systems, and at a relatively low operation temperature of 60 °C. These former measurements have been conducted with the open anode mode, i.e., without partial anode gas recirculation from outlet to inlet, which does not enable correctly considering impurity accumulation and reactivity and their effect correctly for automotive PEMFC stacks.

The hydrogen quality requirements for PEMFC road vehicles in ISO 14687:2019 have largely been developed, by using a safety factor assuming the maximum of the 500-fold accumulation of impurity [10]. However, the accumulation is difficult to simulate, because it is affected by the substance's reactivity, water solubility, membrane permeability and adsorption properties [10]. Thereby, more contamination studies with operation representative of automotive conditions, as in [10, 11], are needed to revise the impurity concentration limits of the hydrogen fuel standard.

There is no separate limit for toluene in the current ISO 14687 standard, but all hydrocarbons, except CH₄, have a common limit of 2 ppm (C1 basis). Therefore, in case no other hydrocarbons are present in the hydrogen fuel, a maximum of 2/7 ppm toluene is currently allowed. A separate, correct and evidence-based limit for toluene, as well as to other LOHC-derived contaminants, is required to facilitate the use of LOHCs in H₂ transportation and storage for automotive use.

In this paper, the results of fuel cell contamination studies with 10, 20, and 50 ppm toluene in hydrogen are presented. In addition, measurements with a mixture of 50 ppm toluene and 0.5 ppm CO are reported. The measurements were

conducted with an automotive-type 5-cell short stack, anode recirculation mode and high fuel utilization (~98%). The results show that the short-term effect of toluene on fuel cell performance is negligible with 10 and 20 ppm concentrations of toluene. The combined effect of 50 ppm toluene and 0.5 ppm CO was smaller than the combined overvoltage from two impurities alone. The enrichment factor in these measurements was from 41 to 52.

2 Experimental

The methodology for studying the effect of toluene had been developed so that for each measurement a baseline, a contamination and a recovery phase were recorded, and online gas samples were analyzed with a gas chromatogram, similar to Bender et al. [5]. The effect of toluene on the PEMFC was compared with the effect of well-studied impurity CO, as in the study of Narusawa et al. [12]. The similar methodology has been described in the study of Viitakangas et al. [11]. A measurement with 2 ppm CO was conducted as a reference measurement for easy monitoring of state of health of the stack. This reference measurement was conducted a day before and a day after each impurity level. The CO concentration was chosen so that a clearly measured voltage drop was seen in a moderate period. Large voltage drops in CO poisoning cause irreversible degradation for the cells. A 50 mV average cell voltage drop was used as a stop criteria for the measurement, to assure no irreversible degradation would take place.

The time of one measurement for reversible impurity has been set at four hours, to correspond to approximately the run time of one full fuel tank of H₂. After each measurement, a shutdown procedure is applied, where oxygen is introduced to the anode to oxidize the adsorbed carbon monoxide (and other possible irreversible contaminants). This approximately 1 h procedure is conducted to clean the platinum catalyst surface and assure similar state of catalyst at the beginning of each individual measurement. Gottesfeld and Pattford [13] first showed the efficiency of injecting O₂ into the anode hydrogen flow to remove the adsorbed CO, and later, introducing air during stops have also been successfully used to recover performance [14].

The measurements were conducted in a Greenlight G60 test station, equipped with an in-house built recirculation system for anode gas (see Figure 1). The circulation system included two KNF PM24927-86.12 pumps factory-modified for hydrogen use in parallel, Vaisala HMT310 humidity and temperature sensors and First Sensor 8000 and 7000 series pressure transmitters. The anode was run at the dead-end mode, with 200 ms purge at 1 min^{-1} frequency. The stack was a 5-cell short stack from Powercell, with active area of 195 cm^2 for each MEA and anode platinum loading of $0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The same stack was used for all measurements. The measurements were run at steady state condition at 0.6 A cm^{-2} , at 80 °C, inlet dew points were 64 °C and 45 to 51 °C, and inlet pressures 22 kPa_g

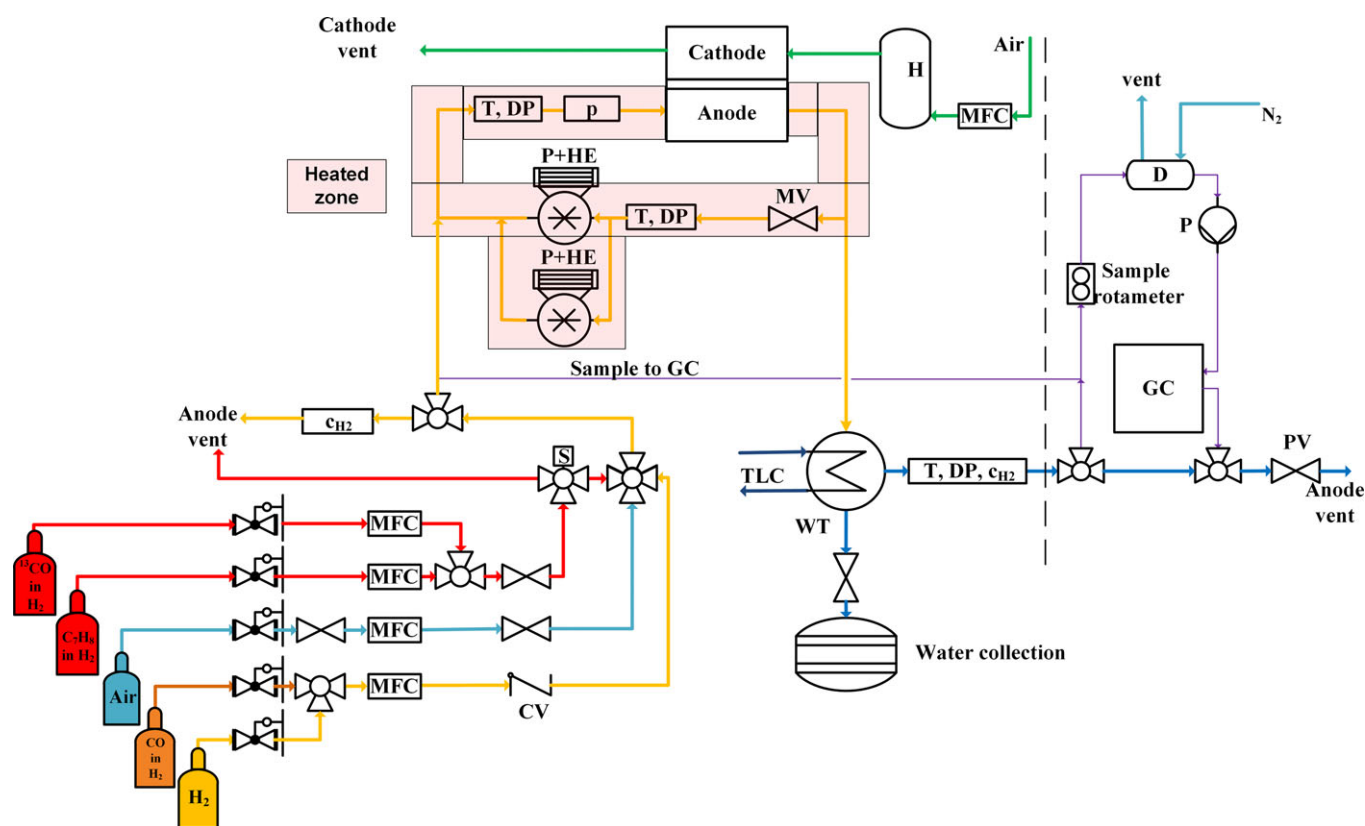


Fig. 1 Schematic of the measurement system for toluene contamination studies. c_{H_2} : hydrogen concentration sensor, CV: check valve, D: dryer, DP: dew point sensor, GC: gas chromatograph, H: humidifier, MFC: flow controller, MV: manual valve, p: pressure sensor, P: pump, PV: purge valve, P+HE: pump and heating element, R: rotameter T: thermocouple, TLC: thermostatic liquid circulator, WT: water trap.

and 29 kPa_g on the cathode and anode, respectively. The air stoichiometry was two and data logging frequency was 1 s⁻¹.

The hydrogen gas was grade 5.0 (with purity $\geq 99.999\%$) and the toluene-hydrogen mixture was diluted from 500 ppm toluene in hydrogen gas, and CO hydrogen mixture from 100 ppm CO in a hydrogen gas bottle within the test system. The inlet concentrations of impurities in feed gases were verified with a gas chromatogram from each repetition of the impurity measurements, while outlet gases were monitored during other measurements. Air fed into the fuel cell was compressed, and filtered air and the hydrogen fed into the fuel cell bypassed the G60's humidifier in order to avoid adding extra impurities from the humidifier's water.

The gas chromatogram device used to measure CO, CO₂, CH₄, benzene (C₆H₆), toluene (C₇H₈) and methyl cyclohexane (C₇H₁₄) was equipped with a flame ionization detector (FID, a capillary column, 30 m × 0.32 mm × 0.25 μm), and thermal conductivity detector (TCD) and pulse discharged helium ionization detector (PDHID with a packed Shincarbon column, 2 m × 1/8" × 2 mm) detectors. The analysis time interval was 14 min. The initial oven temperature, 40 °C, was maintained for 2 min, after which the temperature was ramped up to 120 °C at the rate of 10 °C min⁻¹.

The gas chromatogram was calibrated with the calibration gas of concentrations 98.7 ± 2 ppm and 96.9 ± 2 ppm of toluene and benzene, respectively. For methyl cyclohexane calibra-

tion, a sensitivity factor [15] and molecular masses were used to calculate the correlation between the methyl cyclohexane peak area and concentration.

Each measurement was started with an automated start-up procedure. The start-up procedure included pre-heating the stack to 45 °C while purging the anode and cathode with nitrogen, and then switching to reactant gases and a stepwise increase of the load to the nominal value and waiting for the stack to reach the operation temperature. After the start-up, the stack was run with pure hydrogen for 30 min to obtain the baseline. Then the impurity was fed into the stack for four hours, or as long until an average cell voltage drop of 50 mV was reached. A 30 min recovery with pure hydrogen was run after the contamination measurements for 50 ppm toluene. An automated shutdown procedure with a controlled air purge on the anode side was executed after each measurement to clean the catalyst. A safe air purge was realized so that first, the cathode and anode were inertized by purging with nitrogen. Then, 10 smLPM of air was fed to the anode for approximately an hour. After the air purge, the anode and the cathode were flushed again with nitrogen, and the fuel cell was left in a nitrogen environment overnight.

The measurement sets with 10, 20, and 50 ppm toluene in hydrogen and mixed impurity of 50 ppm toluene and 0.5 ppm CO in hydrogen, referred as measurement set [a], [b], [c] and [d], respectively, were all run similarly: First, a ref-

erence 2 ppm CO contamination was run, followed by two consequent measurements with the toluene or mixture concentration level in question, measurements (1) and (2), then another reference 2 ppm CO measurement, and finally, a reference measurement with pure hydrogen. The measurement sets were run in order of concentration level starting with the lowest impurity concentration [a] and finishing with mixed impurity measurement set [d]. One measurement was conducted per one workday, after which the test system was let to cool down over the night, to assure a similar start state for each measurement.

The total hydrogen fuel utilization was approximately 98% in all the measurements, calculated as explained in the following. The total hydrogen fuel utilization was estimated by treating a purge as a “constant bleed” at the anode outlet. In the following, superscript *r* refers to the hydrogen recirculation loop *f* to feed gas to fuel cell anode, *p* to purged hydrogen fuel considered a bleed, and *c* to consumed and/or permeated gas in the fuel cell stack. Assuming that the only reaction with toluene is



and the toluene (tol) methyl cyclohexane (MeCH) balance is

$$\dot{n}_{\text{tol}}^f = \dot{n}_{\text{tol}}^p + \dot{n}_{\text{MeCH}}^p \quad (2)$$

Then, neglecting hydrogen permeation through membrane and other possible hydrogen losses (≈ 0), from hydrogen balance

$$y_{\text{H}_2}^f \dot{n}^f = y_{\text{H}_2}^{p'} \dot{n}^{p'} + \dot{n}_{\text{H}_2}^c \quad (3)$$

where $y_{\text{H}_2}^f$ and $y_{\text{H}_2}^{p'}$ are molar hydrogen fractions in fuel and purged gas before purge valve, purged gas, $\dot{n}^{p'}$, can be solved and introduced into the toluene methyl cyclohexane balance

$$y_{\text{tol}}^f \dot{n}^f = y_{\text{tol}}^p \dot{n}^p + y_{\text{MeCH}}^p \dot{n}^p \quad (4)$$

Here, however, we need to consider that the gas going into the gas chromatograph, \dot{n}^p , has a lower humidity (considered as dry gas) than the gas at the point of a hydrogen concentration sensor, $\dot{n}^{p'}$:

$$\dot{n}^p = \left(1 - \dot{n}_{\text{H}_2\text{O}}^{p'}\right) \dot{n}^{p'} \quad (5)$$

Now, fuel utilization (*FU*)

$$FU = \dot{n}_{\text{H}_2}^c / \dot{n}_{\text{H}_2}^f \quad (6)$$

can be solved

$$FU = 1 - \left(y_{\text{H}_2}^{p'} y_{\text{tol}}^f\right) / \left(\left(1 - y_{\text{H}_2\text{O}}^{p'}\right) y_{\text{H}_2}^f \left(y_{\text{tol}}^p + y_{\text{MeCH}}^p\right)\right) \quad (7)$$

The enrichment factor, γ , is

$$\gamma = \left(y_{\text{tol}}^p + y_{\text{MeCH}}^p\right) / y_{\text{tol}}^f \quad (8)$$

and therefore *FU* can also be written as

$$FU = 1 - \gamma^{-1} \left(y_{\text{H}_2}^{p'} y_{\text{tol}}^f\right) / \left(\left(1 - y_{\text{H}_2\text{O}}^{p'}\right) y_{\text{H}_2}^f\right) \quad (9)$$

The above fuel utilization estimation assumes that the gas in the pipe volume before the purge valve and between gas chromatograph T-couplings, Figure 1, is fully replaced with the stack's anode outlet gas during the purge. If the volume is partly filled with fresh hydrogen fuel, the measured enrichment, Eq. (8), is measured slightly smaller than in reality, and therefore, *FU* is calculated slightly smaller. On the other hand, a purge that does not flush the piping completely from the anode recirculation T-coupling to the anode vent causes only a time shift to *FU* calculation. Therefore, using Eq. (9) to calculate total hydrogen fuel utilization should not overestimate *FU*.

Assuming that all the formed methyl cyclohexane and all the unreacted toluene come out within the purged gases, and that reaction in Eq. (1) is the only reaction which occurs within these species, then the extent of reaction is

$$\alpha = y_{\text{MeCH}}^p / \left(y_{\text{tol}}^p + y_{\text{MeCH}}^p\right) \quad (10)$$

The extent of reaction, α , was calculated to be approximately 99.8%, Table 1, which implies the almost full conversion of toluene to methyl cyclohexane inside the stack. This result is similar to previous studies where a full or almost full conversion has also been observed [4, 5, 8].

Table 1 Inlet and outlet concentrations of toluene (C_7H_8) and methyl cyclohexane (C_7H_{14}) and extent of reaction of Eq. (1), α , for measurements with 10 ppm toluene [a], 20 ppm toluene [b], 50 ppm toluene [d], and 50 ppm toluene with 0.5 ppm CO [d]. The outlet concentrations are analyzed from the first contamination measurement (1) and the inlet concentration from the repetition contamination measurement (2) for contamination concentrations [a–d].

	10 ppm toluene measurement [a]		20 ppm toluene measurement [b]		50 ppm toluene measurement [c]		50 ppm toluene + 0.5 ppm CO measurement [d]	
	C_7H_8 / ppm	C_7H_{14} / ppm	C_7H_8 / ppm	C_7H_{14} / ppm	C_7H_8 / ppm	C_7H_{14} / ppm	C_7H_8 / ppm	C_7H_{14} / ppm
In (2)	12.6 ± 0.3		24.8 ± 0.5		62.3 ± 1		67.3 ± 1	
Out (1)	1.3 ± 0.03	510 ± 20	2.7 ± 0.06	1,190 ± 30	6.5 ± 0.2	3,250 ± 100	7.2 ± 0.2	2,800 ± 100
α / %	99.7 ± 0.01		99.8 ± 0.008		99.8 ± 0.008		99.7 ± 0.01	

3 Results and Discussion

No performance effect was seen with 10 or 20 ppm toluene measurements, see Figure 2. In the contamination measurement with 10 ppm toluene, the voltage drop was 7 mV within 4 h, which is similar to the voltage drop with pure hydrogen, 5 mV, implying a negligible contamination effect. The effect of 20 ppm toluene was in the same range of the effect with 10 ppm toluene. In the contamination measurement with 20 ppm toluene, the voltage drop was also approximately 7 mV in 4 h. The measured methyl cyclohexane concentrations fluctuate notably (Figure 2), which is partly due to the fluctuations in the purged gas. The amount of the purged gas varies, due to the variations in the flow resistance along the channels [16]. All the average cell voltages in Figures 2–4 have been drawn as centered moving average of 11 s for enhanced readability. The average cell voltage drops have been depicted relative to the average of the first 30 s of each baseline measurement. The change of noise level that is noticeable, e.g., in Figure 2 around 70–80 min is due to a problem with cathode

pressure control of the test station, which was diagnosed after the measurements, and is not an effect of impurity.

The reversible degradation which is seen during all of the measurements, and that is the most pronounced in reference measurements without impurities in the fuel feed (Figure 2) is caused by, e.g., the CO poisoning which originates from the electrochemical formation of CO from CO₂ [17,18], but also from the irreversible carbon corrosion at the anode [13]. The CO₂ which is reduced to CO comes both, permeating through the membrane from the cathode and, in very low quantities, from hydrogen fuel. Atmospheric air contains 412 ppm CO₂ [19] and there is no CO₂ removal in our air purification system. In our measurements, the maximum CO₂ concentration on the anode outlet with recirculation commonly varied between 200–300 ppm.

In the measurement with the highest contamination concentration, 50 ppm toluene, a severe voltage drop was seen, see Figure 3. The first 50 ppm measurement was run for a full 4 h, with a voltage drop of 37 mV. The second 50 ppm measurement was terminated when 50 mV was reached after

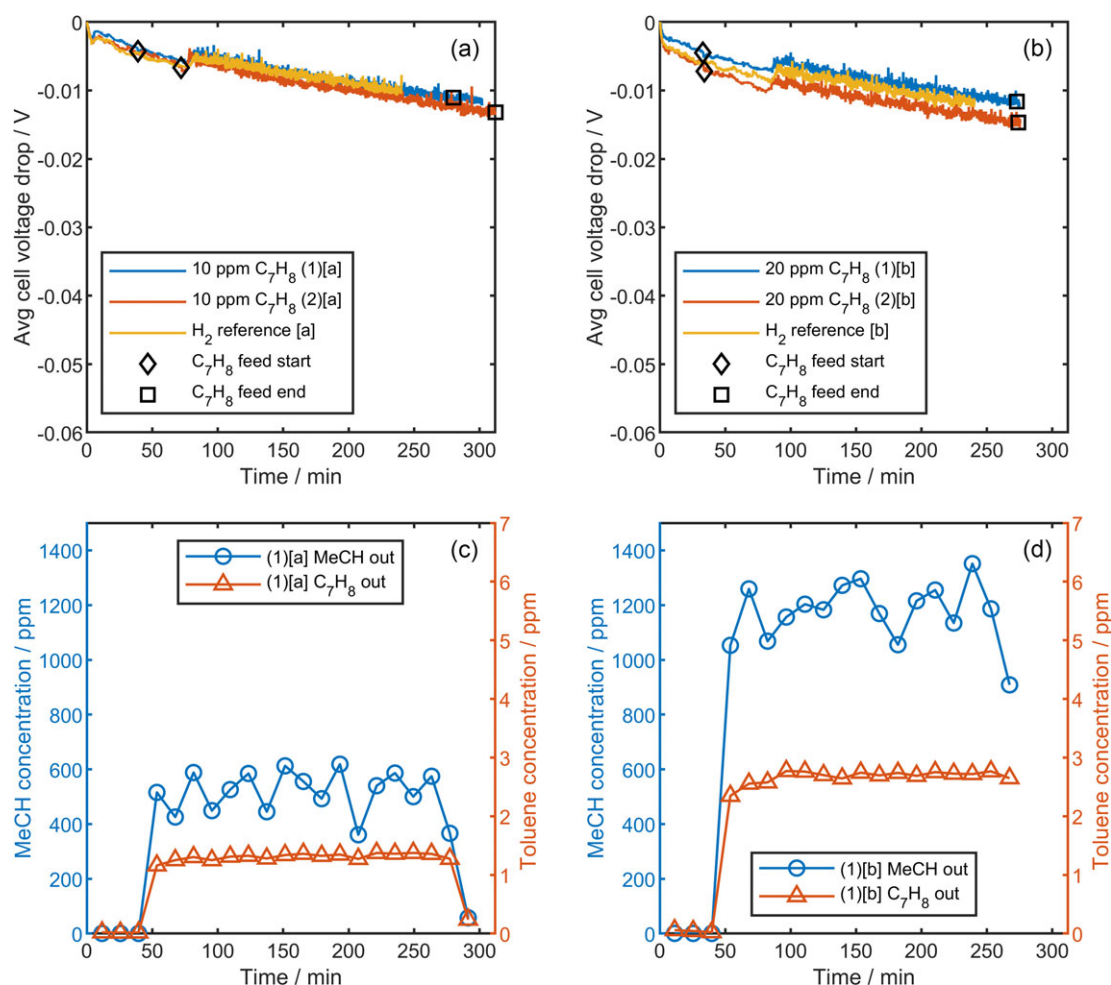


Fig. 2 Voltage drops of cell averages in (a) 10 ppm and (b) 20 ppm toluene contamination and H₂ reference measurements. Measured outlet concentrations of methyl cyclohexane (MeCH) and toluene (C₇H₈) are presented below average voltage figures, (c) corresponding the first measurement with 10 ppm toluene, (1) [a], and (d) corresponding the first contamination measurement with 20 ppm toluene, (1) [b].

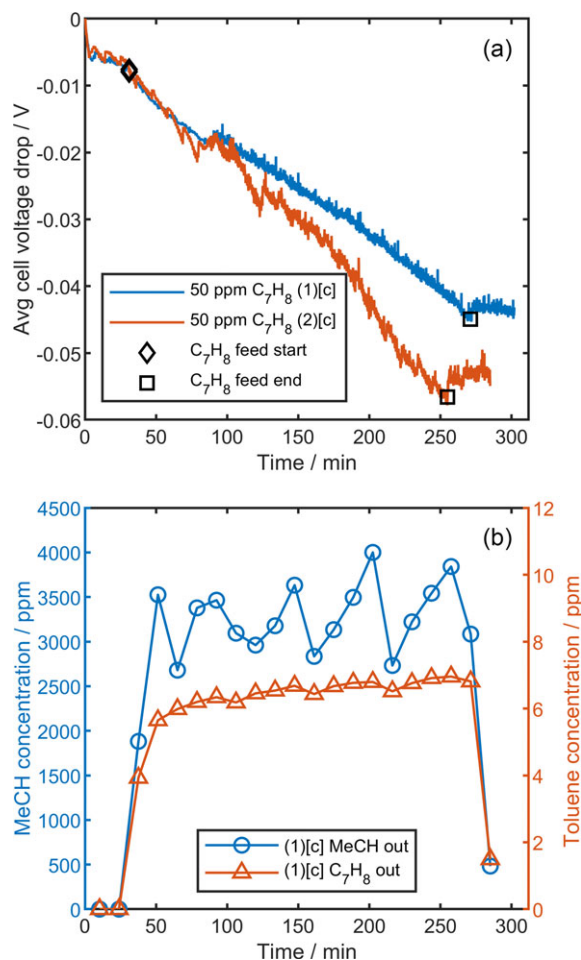


Fig. 3 (a) Voltage drop of cell average in 50 ppm toluene contamination and (b) methyl cyclohexane and toluene concentrations at the outlet in the first 50 ppm toluene contamination measurement, (1) [c].

operation with the contamination of 3h 44 min. With anode gas recirculation, the methyl cyclohexane at the anode outlet was over 3,000 ppm.

When measurements were conducted with mixed impurities of 50 ppm toluene and 0.5 ppm CO, a clear effect on performance was seen, as shown in Figure 4. With mixed impurities, 50 mV voltage drop was reached faster, in 2 h 47 min and in 1 h 40 min, compared with 41 mV voltage drop in 4 h with 0.5 ppm CO solely. Due to notable degradation of cell no 1 at this point, the performance of the cell 1 was seen to drop steeply soon after the impurity feed was started. Therefore, the average cell voltages for the mixed impurity measurement set were calculated only with cells 2–5. An immediate, but very small recovery was observed when gas was changed from 50 ppm toluene to pure hydrogen, 2 and 4 mV for first and second measurement, respectively. In case of mixed impurity, the recovery was 5 mV for both measurements.

The effect of impurity mixtures cannot be expected to be the sum of the effects of two single impurities. Previous studies have shown that the effect of impurity mixtures can be higher or of similar magnitude, and/or have different overvol-

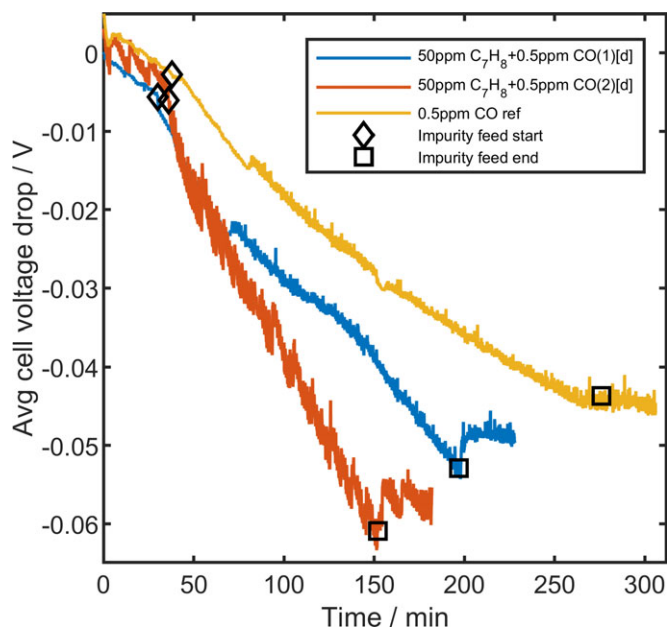


Fig. 4 Voltage drop of cell average in 50 ppm toluene (C_7H_8) + 0.5 ppm CO contamination measurements, (1) [d] and (2) [d]. Average cell voltage drops are calculated with cells 2–5, due to unknown degradation of cell 1.

tage-time behavior than the effects of the same impurity concentrations solely [4, 8, 9]. In these measurements, the CO with the toluene mixture had a smaller overall effect than the calculated sum of the effects. This is probably due to the larger size of toluene and methyl cyclohexane molecules compared to H_2 . Therefore, after the partial coverage of CO, locally, there may not be sufficient adjacent catalyst sites available for toluene. However, smaller hydrogen molecules may still adsorb to the sites. The measured methyl cyclohexane concentrations on the anode outlet were lower in the measurements with mixed impurities than with 50 ppm toluene only, 2,800 ppm vs. 3,200 ppm, which supports this assumption. Further studies of impurity mixtures with low-loading anodes are needed.

The average inlet and outlet concentrations of toluene and methyl cyclohexane are presented in Table 1, measured by gas chromatogram. The overall errors have been evaluated as the root sum squared method. For the error of the average values of gas chromatograph peaks, the standard deviations of the mean have been calculated. The enrichment ratio in these measurements was from 41 to 52, calculated with the outlet sum of toluene and methyl cyclohexane that was expected to be formed from toluene with a 1:1 ratio, according to Eq. (1).

At the beginning of the measurements, the CO reference measurements with 2 ppm CO mixed with pure hydrogen showed a voltage drop of a 50 mV in approximately 1 h, see Table 2. By the end of the measurements, 50 mV voltage drop was reached in half an hour. The evolution of irreversible degradation is also visible when the baselines of CO reference measurements are compared (Figure 5).

It also must be noted that during the toluene impurity measurements, the stack performance was not recovering as

Table 2 The duration of 2 ppm CO reference measurements. [a] refers to 10 ppm toluene series, [b] to 20 ppm toluene series, [c] to 50 ppm toluene series, and [d] mixture of 50 ppm toluene and 0.5 ppm CO series. (1) refers to the CO reference measurement before toluene impurity measurement of each measurement set [a–d], and (2) to the CO reference measurement after the toluene contamination measurements of the contamination level in question [a–d]. Duration is the time from the beginning of the impurity feed to the 50 mV average cell drop (after which the impurity feeding is stopped).

Measurement	Duration to 50 mV drop / min
CO 2 ppm (1) [a]	65
CO 2 ppm (2) [a]	59
CO 2 ppm (1) [b]	59
CO 2 ppm (2) [b]	60
CO 2 ppm (1) [c]	33
CO 2 ppm (2) [c]	34
CO 2 ppm (1) [d]	27
CO 2 ppm (2) [d]	27

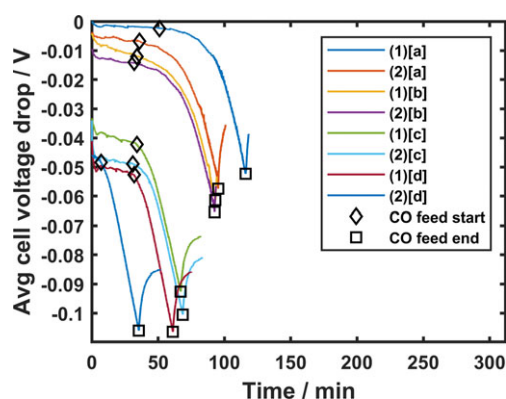


Fig. 5 Voltage drops of cell average in all 2 ppm CO reference contamination measurements. [a], [b], [c], and [d], refer to measurement series with 10 ppm toluene, 20 ppm toluene, 50 ppm toluene, and 50 ppm toluene with 0.5 ppm CO, respectively. Zero level baseline is set at the average of the first 30 s of the first reference measurement, (1) [a].

expected during reversible impurity measurements with a shutdown procedure containing an oxidizing cleaning phase. It can be seen, that both 50 ppm toluene and mixture measurements have a similar trend, where the first impurity measurement performs better than the second. Irreversible degradation was clearly observed to occur, especially between the 20 and 50 ppm toluene impurity measurement series. We assume this is related to issues other than toluene contamination, since there was a longer pause in toluene measurements. In Figure 5, it is shown that the performance of the stack was noticeable better in the last 2 ppm CO reference measurement, (2) [b], before the break than in the first CO reference measurement after the break, (1) [c]. In addition, it was seen, that while the cell-to-cell variations were 20 mV on average with pure H₂ in the first two measurement sets, [a] and [b], they grew larger, 35 mV on average with pure H₂, in the last two measurement sets, [c] and [d]. A long-term degradation may derive from the

measurement procedures, emergency shutdown procedure and conditions, or from the measurement setup. In addition, problems arose with the cathode pressure control of the test station, which caused some stepwise changes and small fluctuations in the cathode inlet pressure. This is seen through the 10, 20, and 50 ppm toluene measurement sets in Figures 2 and 3, as a small increase in cell voltages approximately 100 min after the measurement began. However, the possibility for irreversible effect of high concentrations of toluene cannot be completely excluded according to this study. The study of the effect of toluene will be further continued with an improved system and a new, slightly larger stack.

4 Conclusions

In this study, it is shown that the short-term effect of toluene on PEMFC is negligible with 10 and 20 ppm concentrations. With concentration of 50 ppm toluene in hydrogen, a contamination effect was evident. 50 ppm toluene in hydrogen is 175 times the current limit for toluene (total hydrocarbons) in the hydrogen fuel standard. It should also be noted, that with higher fuel utilization which is more close to real automotive operation of PEMFC stacks (99.5%), higher impurity accumulation occurs and lower level of concentration may have a visible effect on the performance.

The measurements have been conducted with a 5-cell automotive PEMFC stack with a test system with the anode recirculation and accumulation of impurities similar to real conditions in automotive PEM stacks and systems. The fuel utilization in the measurements was ~98% with a 40- to 50-fold accumulation of impurities in the recirculation system. These results show that more studies are needed for toluene, as it is possible that it should not be counted as ‘total hydrocarbons’ in hydrogen fuel standard ISO 14687 but could have its own concentration limit instead. For future studies, the reversibility of toluene contamination should be further studied, as well as the long-term effect of toluene on PEMFC automotive stack.

Acknowledgements

The research leading to these results has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement n° 779694 and Business Finland, Finnish Funding Agency for Innovation and Technology. The Joint Undertaking receives support from the European Union’s Horizon 2020 research and innovation programme and Hydrogen Europe and Hydrogen Europe Research.

List of Symbols

α	Extent of reaction
γ	Enrichment ratio
\dot{n}	Molar flow / mol s ⁻¹
y	Molar fraction

Subscripts

H ₂	Hydrogen
H ₂ O	Water
MeCH	Methyl cyclohexane
tol	Toluene

Superscripts

c	Utilized and/or permeated gas in the stack
f	Fuel cell anode feed gas
p	Purged anode gas after GC loop dryer
p'	Purged anode gas

References

- [1] P. T. Aakko-Saksa, C. Cook, J. Kiviaho, T. Repo, *J. Power Sources* **2018**, 396, 803.
- [2] A. Fikrt, R. Brehmer, V.-O. Milella, K. Müller, A. Bösmann, P. Preuster, N. Alt, E. Schlücker, P. Wasserscheid, W. Arlt, *Appl. Energy* **2017**, 194, 1.
- [3] A. Bulgarin, H. Jorschick, P. Preuster, A. Bosmann, P. Wasserscheid, *Int. J. Hydrogen Energy* **2020**, 45, 712.
- [4] S. Dorn, G. Bender, K. Bethune, M. Angelo, R. Rocheleau, *ECS Trans.* **2008**, 16, 659.
- [5] G. Bender, M. Angelo, K. Bethune, S. Dorn, T. Thampan, R. Rocheleau, *J. Power Sources* **2009**, 193, 713.
- [6] X. Wang, P. Baker, X. Zhang, H. F. Garces, L. J. Bonville, U. Pasaogullari, T. M. Molter, *Int. J. Hydrogen Energy* **2014**, 39, 19701.
- [7] K. Kortsdottir, R. W. Lindström, T. Kermarck, G. Lindbergh, *Electrochim. Acta* **2010**, 55, 7643.
- [8] M. Angelo, K. Bethune, R. Rocheleau, *ECS Trans.* **2010**, 28, 169.
- [9] W. Shi, B. Yi, M. Hou, Z. Shao, *Int. J. Hydrogen Energy* **2007**, 32, 4412.
- [10] Y. Matsuda, Y. Hashimasa, D. Imamura, M. Akai, S. Watanabe, *Rev. Automot. Eng.* **2009**, 30, 167.
- [11] J. Viitakangas, J. Itonen, P. Koski, M. Reinikainen, T. A. Aarhaug, *J. Electrochem. Soc.* **2018**, 165, F718.
- [12] K. Narusawa, M. Hayashida, Y. Kamiya, H. Roppongi, D. Kurashima, K. Wakabayashi, *JSAE Rev.* **2003**, 24, 41.
- [13] S. Gottesfeld, J. Pafford, *J. Electrochem. Soc.* **1988**, 135, 2651.
- [14] B. Decoopman, R. Vincent, S. Rosini, G. Paganelli, P.-X. Thivel, *J. Power Sources* **2016**, 324, 492.
- [15] W. A. Dietz, *J. Chromatogr. Sci.* **1967**, 5, 68.
- [16] R. Anderson, L. Zhang, Y. Ding, M. Blanco, X. Bi, D. P. Wilkinson, *J. Power Sources* **2010**, 195, 4531.
- [17] T. Gu, W. K. Lee, J. W. Van Zee, *Appl. Catal. B Environ.* **2005**, 56, 43.
- [18] T. Smolinka, M. Heinen, Y. X. Chen, Z. Jusys, W. Lehnert, R. J. Behm, *Electrochim. Acta* **2005**, 50, 5189.
- [19] National Oceanic and Atmospheric Administration, Recent monthly mean CO₂ at Mauna Loa observatory, Hawaii, USA, can be found under <https://www.esrl.noaa.gov/gmd/ccgg/trends/> (access date: 18.4.2019).