

Fuelling the hydrogen economy

Scale-up of an integrated formic acid-to-power system

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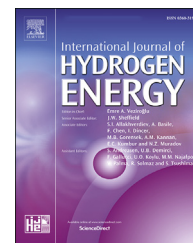
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Fuelling the hydrogen economy: Scale-up of an integrated formic acid-to-power system

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ABSTRACT

Transitioning from fossil fuels to sustainable and green energy sources in mobile applications is a difficult challenge and demands sustained and highly multidisciplinary efforts in R&D. Liquid organic hydrogen carriers (LOHC) offer several advantages over more conventional energy storage solutions, but have not been yet demonstrated at scale. Herein we describe the development of an integrated and compact 25 kW formic acid-to-power system by a team of BSc and MSc students. We highlight a number of key engineering challenges encountered during scale-up of the technology and discuss several aspects commonly overlooked by academic researchers. Conclusively, we provide a critical outlook and suggest a number of developmental areas currently inhibiting further implementation of the technology.

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Introduction

Molecular hydrogen produced from renewable energy is an attractive alternative to current fossil fuels. Hydrogen generation technology has matured significantly over the past decades and is now capable of rapid and highly localized production of clean H₂ from renewable energy sources, e.g., electricity or biomass [1–3]. Besides momentarily unfavorable economics and underdeveloped infrastructure, the practical implementation of the hydrogen economy [4] is significantly

challenged by a relatively slow development of efficient, safe, and scalable storage solutions for gaseous hydrogen [5,6]. Containment strategies such as compression and liquefaction offer attractive volumetric and gravimetric energy densities at cost of significant efficiency losses, while metal-hydrides typically are too heavy for mobile applications and frequently exhibit unfavorable loading/unloading kinetics [7–9].

In 2012 Laurency, Beller, and co-workers demonstrated a highly reversible hydrogen storage system based on Ru-catalyzed formic acid (de)hydrogenation, which was

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appropriately named a ‘hydrogen battery’ [10]. The proposed technology utilized formic acid as a liquid hydrogen carrier that in the presence of a catalyst could be readily decomposed to produce gaseous H_2 with CO_2 as the sole by-product, thus effectively serving as a hydrogen carrier material that in the presence of molecular hydrogen can be converted back to the formic acid (HCOOH, FA) liquid organic hydrogen carrier. The ‘hydrogen battery’ approach based on reversible CO_2 hydrogenation-dehydrogenation enables carbon-neutral hydrogen storage in FA and may play a pivotal role in a future hydrogen economy provided that the required (catalytic) technology can be developed [11–13]. So far a wide range of homogeneous and heterogeneous catalytic systems for both formic acid decomposition and hydrogenation of carbon dioxide to FA have been reported [14–23]. Despite its low gravimetric hydrogen density of 4.4 wt% (compared to 12.6 wt% for its common alternative methanol), the hydrogenation of CO_2 to FA can be accomplished at relatively low temperature and allows for complete atom efficiency [24]. Based on this approach one can envisage automotive applications wherein gasoline is replaced by formic acid and cars are outfitted with fuel cell technology (either Direct Formic Acid Fuel Cells (DFAFC) [25,26] or hydrogen fuel cells, Fig. 1). Pure formic acid is corrosive and has a significantly increased flash point compared to gasoline, resulting in relatively facile handling and thus warrants only minor modifications to current infrastructure. These attractive properties combined with recent developmental leaps in catalytic (de)hydrogenative chemistry of CO_2 to FA renders formic acid an attractive fuel for future automotive applications [27]. Scale-up of catalytic systems demonstrated thus far is associated with a number of yet unresolved engineering challenges that are rarely addressed in the open literature.

Several years ago our group hosted a project for undergraduate students who demonstrated this concept at a miniature scale and ultimately successfully powered a 600 mW model car. This work led to the founding of Team FAST: an independent and multidisciplinary team of BSc and MSc students at Eindhoven University of Technology, working towards a 25 kW power system to serve as a range-extender for a full-scale hydrogen-powered city bus. Afterwards Team FAST [28] transitioned into start-up company DENS [29] (Dutch Energy Solutions) and is actively bringing formic acid power generators to market.

In this work, we describe the important engineering challenges encountered by Team FAST/DENS during scale-up of R&D-scale technologies available in the open literature. We discuss several aspects commonly overlooked by academic researchers and highlight critical developmental areas currently hindering implementation of the described technology.

Reaction and process development

Process development was started with a series of laboratory-scale experiments to gain valuable insight into critical reaction parameters of the catalytic system, i.e., lifetime stability, catalytic activity, and selectivity for carbon dioxide and hydrogen. The latter is especially important considering the low tolerance of hydrogen fuel cells for strong adsorbents such as carbon monoxide that may be formed upon formic acid dehydrogenation and ultimately cause slow degradation of the fuel cell [30]. A small-scale 25 W model car was developed for testing and marketing purposes and was named Formauto Junior (Fig. 2).

The first explored catalyst candidate was an isolated and exceptionally active ruthenium lutidine-derived pincer complex developed in our group [31]. The RuPNP catalytic system (Scheme 1) is capable of low temperature (65 °C) reversible FA (de)hydrogenation in presence of organic bases NEt_3 and DBU. The very high intrinsic activity of this system potentially would allow reduction of equipment sizing and thus drive down the equipment and operational costs. Continuous-flow experiments (i.e., dosage of formic acid at constant rate while measuring gas evolution) quickly revealed a number of difficulties associated with scale-up of a mobile technology based on RuPNP. Despite highly attractive catalytic activity in DMF/ NEt_3 solution, neither the ligand nor the isolated complex is available commercially at sufficient scale, nor could it be generated in-situ from relatively cheap and easily obtainable ruthenium precursors as these are predominantly Ru^{III} salts. In solution RuPNP was found to be highly air sensitive and it quickly lost activity when used in the model car wherein rigorous air exclusion was much more challenging than in a small laboratory reactor. At this stage it was decided that RuPNP was not suitable for scale-up and alternative options were explored.



Fig. 1 – Schematic overview of carbon-neutral implementation of FA-energy storage technology.



Fig. 2 – Formauto Junior: proof-of-concept 25 W model car for testing and marketing purposes.

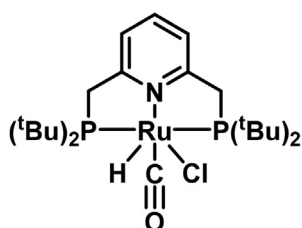
Driven mainly by the economical and engineering considerations, focus then shifted towards an in-situ generated Fe catalyst jointly developed by the groups of Beller and Laurency (Scheme 1) [32]. Major advantages of this system are that it does not rely on noble metals and its very high activity in propylene carbonate (PC), which is regarded a nontoxic and environmentally benign solvent with low vapor pressure [33]. Its low volatility is particularly attractive for mobile applications operated at around 100 °C as it significantly reduces power requirements for condensation of volatilized solvent and consequently directly impacts system cooling duty and overall efficiency. Use of non-toxic and abundant iron in combination with a green and low-energy solvent would present considerable sustainability benefits and increase the attractiveness of the technology with the general public and potential investors. Unfortunately, subsequent studies quickly identified that the particular catalyst is unstable towards water and/or dissolved chloride ions commonly encountered in commercial grade formic acid and it consequently deactivated over the course of about a week in the model car.

High catalytic activity was deprioritized as lack thereof could be compensated through late-stage engineering. Suitability of an aqueous in-situ catalytic system consisting of ruthenium trichloride hydrate metal precursor and TPPTS

ligand was investigated (Scheme 1) [34–36]. At the time this particular catalyst had been in operation for over a year at EPF Lausanne and had been demonstrated to be highly robust [34–36]. Sufficient catalytic activity was found while achieving impressive stability. Advantageously, this system is stable in air, robust, can be readily prepared in-situ from commercially available components at reasonable cost, and shows high selectivity towards H₂ and CO₂ without detectable CO by-product. The relatively high cost of the ruthenium active component compared to cheaper and more abundant iron are effectively offset by the exceptionally high catalyst stability, which potentially would allow long-term operation of the hydrogen generation system without the need for continuous addition of fresh catalyst to retain the desired H₂ output.

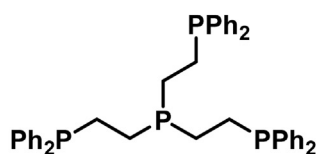
Reintroduction of water as the reaction medium implied solving challenges originating from unacceptable boil-off rates and high cooling duties caused by the high gas flow from the reactor. The use of alternative high-boiling solvents was evaluated. The screening included common organic solvents such as ethylene glycol, DMSO, propylene carbonate, and aqueous mixtures thereof, but neither produced sufficient activity under the selected conditions. Considering the impressive performance reported for Ru catalysts in ionic liquids [37], 1-ethyl-3-methylimidazolium acetate was synthesized and tested, with short experiments at small scale resulting in acceptable performance. Under more realistic conditions, however, solvent degradation led to formation of volatile amines and thus proved incompatible with the sensitive fuel cell downstream [38].

The aqueous Ru TPPTS in-situ catalyst developed by Laurency and co-workers is capable of promoting FA dehydrogenation at 90 °C and high autogenous pressures, which are highly desirable when targeting fuel cell applications to both offset the reduced hydrogen partial pressure in gas mixtures and to obtain increased cell potentials as described by the Nernst equation [39,40]. The team therefore focused on exploring the operation of this catalyst system at elevated pressure to concomitantly provide solutions for a number of associated engineering challenges. High gas-dissolution rates resulted in extensive foaming in small-scale tests, but was virtually absent in the pressurized and larger reactor. Operation at 10–15 bar sufficiently diminished water vaporization to



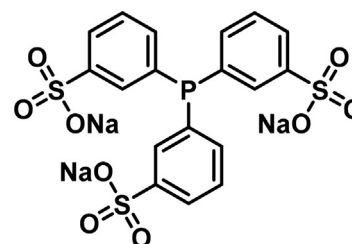
RuPNP

Pidko[31]



Fe(BF₄)₂ · H₂O

Beller/Laurency[32]



TPPTS

RuCl₃ · xH₂O

Laurency[34–36]

Scheme 1 – Catalysts evaluated in this work for scale-up viability.

acceptable levels and reduced estimated continuous heating duties from ~35 kW to just over 1 kW. Pressurization furthermore afforded an attractive reduction of equipment size, which at maximum capacity consumes approximately 1 l of neat >95% FA per minute and consequently produces a large quantity of ~1300 Nl gas per minute ($H_2 + CO_2$) to prevent bottlenecking the 25 kW hydrogen fuel cell. Efficient G/L separation is accomplished upstream to the fuel cell with a cyclone separator, effectively reducing reaction mixture losses and controlling residual gaseous formic acid levels to an estimated 10 parts per billion.

Additional engineering was required for successful integration of the commercial fuel cell system. Most modern fuel cells remain highly sensitive to traces of carbon monoxide and thus demand very high purity hydrogen (<10 ppm CO), while maximum allowed levels for carbon dioxide are typically much less strict. In sharp contrast to the original research [34–36] studies where the CO by-product was not formed in significant quantities, the tests on the scaled-up system produced up to 200 ppm CO with levels decreasing at higher temperatures, suggesting possible involvement of the water-gas-shift reaction. Two possible solutions were therefore envisaged, namely; (i) selective CO oxidation, or (ii) CO methanation. Preferential catalytic oxidation (PROX) to carbon dioxide generally operates at temperatures below 200 °C and requires a co-feed of air or O_2 as the oxidant [41,42]. Catalytic methanation [43–45] relies only on H_2 as the reductant, and was therefore deemed the most attractive technology for implementation. Methanation was selected despite higher temperatures required (~230 °C) and concomitant emission of methane, which is a highly potent greenhouse gas [46]. After methanation the stripped and cleaned gas-stream gets humidified before entering the PEM fuel cell to protect the Nafion polymer membrane and ensure efficient operation. An afterburner-system was integrated downstream of the fuel cell to remove residual methane and unconverted hydrogen and enabled some degree of heat recovery before the effluent is exhausted to the atmosphere.

System overview, start-up, and operation

The integrated system is shown in Figs. 3 and 4 and schematically depicted in Fig. 5. As previously described, the overall system is operated in such a manner to not endanger or bottleneck the sensitive and expensive fuel cell. Formic acid is pumped from the storage tank and converted into carbon dioxide and hydrogen gas in a continuously stirred tank reactor (CSTR). Excess water and formic acid is condensed out and returned to the reactor system. The gaseous stream is stabilized by a backpressure regulator (BPR) and is fed to the catalytic methanation reactor for CO removal, humidified, and subsequently converted into electricity in the fuel cell. Remaining gases predominantly consisting of carbon dioxide are exhausted to the atmosphere.

A fuel cell bypass is available to accommodate heating of the reactor with hot gases and thus decrease electric heating demands when required. Cold start-up of the system can be performed using electricity stored in batteries or with residual hydrogen in the system, requiring ~500 Nl H_2 to heat the

reactor to the required 90 °C. Operation at 80 °C would have facilitated improved heat integration and thus overall system efficiency, but could not be realized due to maximum productivity constraints of the selected catalytic system.

The system is highly responsive to changes in formic acid mass flow rate and accommodates changes within seconds to a minute. This is in contrast to the small-scale laboratory experiments, which frequently took several minutes to reach steady state in outlet gas flow rate without flow-stabilization from the back-pressure regulator. At start-up there is no formic acid present in the reactor and the catalyst readily converts all FA fed until input/output steady state is reached. When the catalyst is saturated it is critical to actively and precisely control formic acid conversion rates (i.e., to not overfeed) to prevent build-up of formic acid in the reactor caused by the bottlenecked catalytic system. This undesirable situation is easily and effectively prevented by selecting operating conditions away from the maximum to ensure sufficient headspace. Accurate temperature control within several °C of effluent gas flows is critical and must remain stable to prevent cathode/anode misbalances in the fuel cell, which could damage the equipment by short-circuiting and excessive wearing.

Results of a steady-state FA-dosage experiment in the up-scaled FA-to-power system are shown in Fig. 6. The reactor contents were pre-heated to a reaction temperature of 110 °C before addition of FA was started to ensure immediate start of the dehydrogenation reaction. As described, virtually instantaneous response in gas evolution rates was observed upon both increasing and decreasing FA feed flowrates. Quantitative steady-state conversion of formic acid was achieved with a total Ru-loading of 0.695 mol, resulting in a steady-state turnover frequency (TOF) of 484 h^{-1} . Minor oscillations are observed in measured effluent gas flows after the back-pressure regulator, which are introduced by the PID-controller actively managing reactor temperature. Full system shutdown is achieved minutes after FA-dosage is stopped.

Remaining challenges

Laboratory-scale experiments are customarily performed with high purity formic acid ($\geq 95\%$). In contrast, large-scale commonly demands utilization of technical grade chemicals due to the unfavorable economics of high quality feeds and possibly restricted availability at scale. As previously discussed, pronounced catalyst deactivation was observed for the Fe-system due to impurities present even in commercial >99% pure FA. The particular chemistry and reactor configuration does not readily facilitate separation or concentration of the catalytic liquid phase, thus necessitating pure and highly concentrated FA. Utilization of 85% formic acid leads to continuous dilution of the catalyst solution and volume build-up by the high water content, ultimately causing the reactor to overflow. Furthermore, use of 85% formic acid reduces energy density and overall system efficiency. Although economically attractive, this approach significantly decreases time between turnarounds and increases operational cost. Viable engineering solutions may be developed to remove water from the

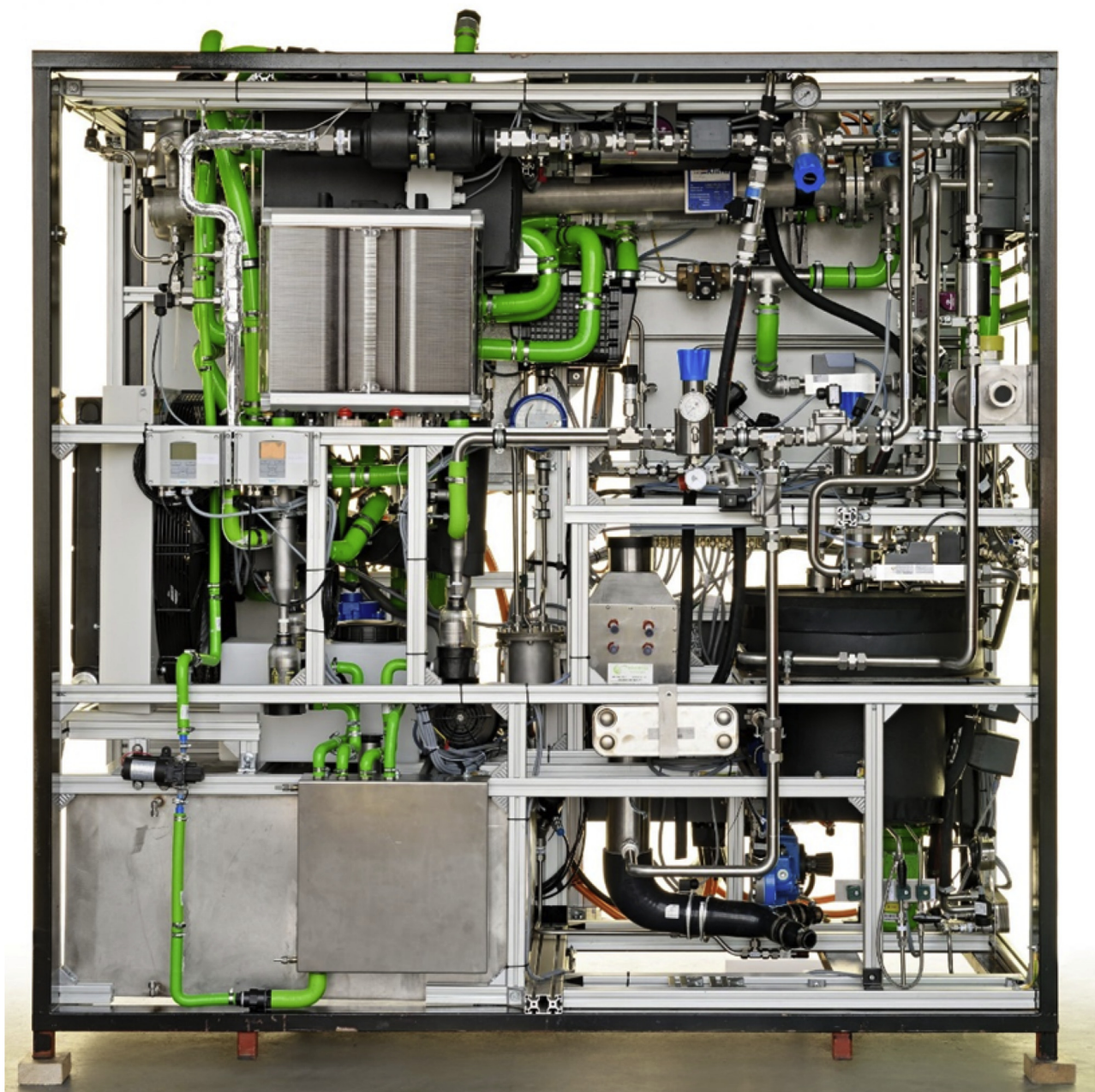


Fig. 3 – Integrated 25 kW formic acid-to-power system.

solution, *e.g.*, use of solvent-selective nanofiltration [47,48] or implementation of a highly selective heterogeneous formic acid dehydrogenation catalyst [49–51]. Such improvements would greatly reduce barriers hindering widespread adoption of FA-based on-board hydrogen storage systems.

CO₂ capture and storage (CCS) is required to establish true carbon-neutral operation. Implementation of onboard CCS, however, remains highly challenging due to the prohibitive energy requirements of gas compression and large spatial footprint of amine-based CO₂-adsorbents, both of which are particularly problematic for mobile applications. However, opportunities remain for localized capture at highly concentrated point sources and centralized collection of 400–600 ppm atmospheric carbon dioxide [52–55]. While

currently challenging, technological breakthroughs may enable sufficiently dense storage and close the carbon cycle for regenerative liquid organic hydrogen carrier (LOHC) energy storage systems [56–61].

A particularly attractive concept for the widespread distribution of FA with possible integrated CCS was recently proposed by Müller and co-workers to enable hydrogen-powered mobile applications at high pressures of >700 bar while circumventing typical mechanical compression losses [62]. In their vision high pressure H₂ is produced at fuel stations via FA dehydrogenation systems capable of operating under very high autogenous pressures, *e.g.*, Laurency's Ru TPPTS system [34–36] and Kawanami's Ir-complex [63]. Beneficially, on-site carbon capture can be integrated to



Fig. 4 – Implementation of 25 kW system in full-scale hydrogen powered city bus.

prevent its emission to the atmosphere and thus close the all-important carbon balance. Thus, green synthesis of FA remains highly desirable and several pathways are currently under development, *e.g.*, production from biomass [64,65] and various strategies based on hydrogenation technology [66–70].

Lastly, economic viability remains a major hurdle for the wide-spread utilization of the FA-based hydrogen storage systems in mobile applications because of the excessively high CAPEX and OPEX investments currently required for the technology described herein. Team FAST/Dutch Energy Solutions (DENS) estimates a total upfront system cost of €100,000, with the fuel cell system approximately contributing 10% and the noble metal catalyst roughly 1%. Following the economic

evaluation reported by Eppinger and Huang [27], a COF value (TOF normalized catalyst cost) of 2.2 is found for the described catalytic system [71]. The reduction of two orders of magnitude compared to Eppinger and Huang's calculation (COF = 384 for $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$ and TPPTS) at \$250,000/mol) is achieved by substitution of the Ru-precursor with widely available $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and purchasing chemicals in bulk. Besides catalyst cost, formic acid availability and price remain critical. In this regard DENS has set a price target for 99% formic acid at €400/\$450 per ton to enable economically viable operation at current European energy prices. Disruptive novel and highly efficient synthetic routes are required for such a significant cost reduction, again highlighting the critical role of R&D in bringing new and sustainable energy technologies to market.

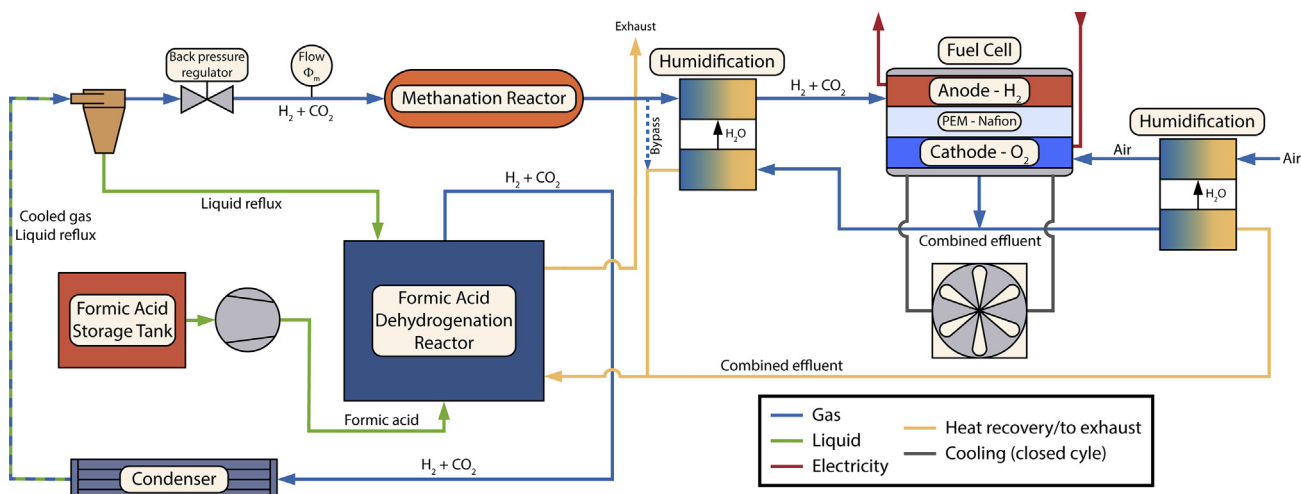


Fig. 5 – Flow diagram for 25 kW formic acid-to-power system.

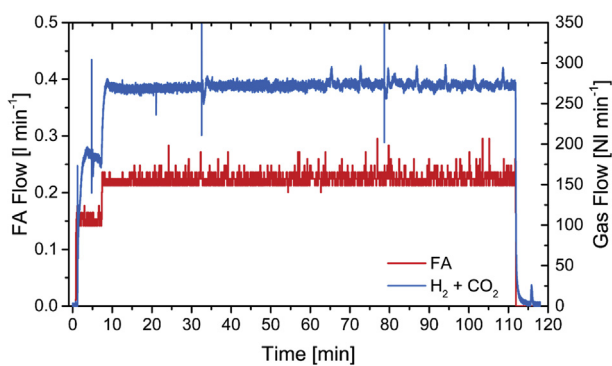


Fig. 6 – Steady-state test in 25 kW standalone system at 110 °C with 0.695 mol Ru. TOF = 484 h⁻¹.

Conclusion

Formic acid was employed as a liquid organic hydrogen carrier to power a 25 kW integrated and compact formic acid-to-power system to power a full scale city bus or serve as a standalone carbon-neutral electricity generator. A detailed post-mortem engineering analysis returned several key engineering challenges encountered during scale-up of the technology described herein. CO present at ppm-levels was successfully removed from the gas stream by methanation, a strategy we believe is generally applicable and allows less-selective, yet highly stable and active dehydrogenation catalysts to become attractive candidates for fuel-cell applications. High intrinsic catalytic activity was found to have little impact on the viability of the developed technology, whereas availability and stability of the utilized catalytic solution were found to be of critical importance for the realization of an onboard formic acid dehydrogenation system. In fact, catalytic activity of the system presented herein is three orders lower compared to the most active Ru and Ir systems available in open literature, yet its high stability renders scale-up feasible. Critical hurdles towards commercial and practical implementation were identified to be availability, purity, and price of the required formic acid feedstock, aspects not commonly addressed by academic researchers. Successful introduction and operation of catalytic FA decomposition systems requires the availability of highly pure FA feeds to avoid continuous dilution of liquid phase, which is not readily concentrated onboard. Tolerance of the catalytic solution towards potential inorganic and organic contaminations present in the feed is key towards ensuring long-term catalytic stability and ultimate commercial viability of the formic acid-to-power technology described herein.

Declaration of interest

Declaration of interests: RvP, TW, EAP: none. TS is an employee of Dutch Energy Solutions B.V.

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