

# Decentralized City District Hydrogen Storage System based on the Electrochemical Reduction of Carbon Dioxide to Formate

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**Abstract**—High fluctuations of renewable energy sources, such as wind and solar energy, require storage capacity to maintain supply reliability. For long term storage energy carriers to substitute fossil fuels must be found. The reduction of carbon dioxide to liquid substances such as formic acid or formate with electrons from renewable energy sources seem to be a promising approach. This paper tries to find answers for the following question: Under which conditions is it possible to use electrochemical carbon dioxide reduction to formate as urban seasonal energy storage?

**Index Terms**—Electrochemical carbon dioxide reduction, energy storage, formate, liquid hydrogen carrier, seasonal city district storage

## I. INTRODUCTION

In a future society independent of fossil energy carriers, a substitute energy carrier must be found. A higher integration of renewable energy requires grid connected storage systems to balance fluctuations. Hydrogen, produced with water electrolysis, which is transformed back to water in fuel cells releases electricity and heat. This is a fully renewable way to provide energy for mobile and stationary applications. Water electrolysis is also suitable to balance fluctuations of the renewable energy production. But as hydrogen has some invincible deficits when stored as a gas, some new possibilities to store the chemical energy of hydrogen must be investigated.

A promising approach is to transform hydrogen to liquid chemical compounds. Liquid energy carriers have the major advantage that people are used to their application and they could easily be transported from where they were produced to where they are needed still using existing pipelines or rail, road or ship transportation infrastructure. For now, some research has been executed investigating liquid hydrogen storage compounds for an efficient hydrogen infrastructure

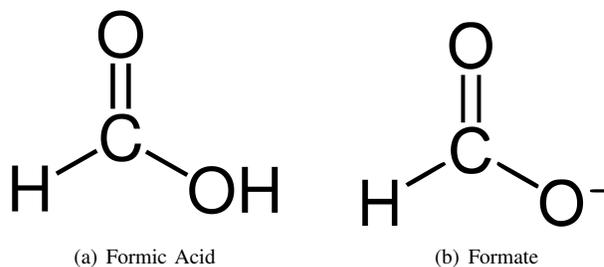


Fig. 1. Molecular Structure of Formic Acid and Formate

[1]–[6].

TABLE I  
GRAVIMETRIC HYDROGEN DENSITIES OF FORMIC ACID AND POTASSIUM FORMATE

Substance	Chem. Formula	Grav. H <sub>2</sub> Density (wt%)
Formic Acid	HCOOH	4.35
Potassium Formate	K <sup>+</sup> HCOO <sup>-</sup>	1.19

As another liquid substance suitable for hydrogen storage formic acid becomes more present in research, as it is non-toxic and easy to store [7], [8]. Formic acid is the simplest carboxylic acid. Formic acid salts are called formate. Its molecular structure is shown in figure 1. Table I outlines the chemical formula and the gravimetric hydrogen density of formic acid and potassium formate.

Two possible routes for the production of formic acid or formate exist with regard to renewable energy sources:

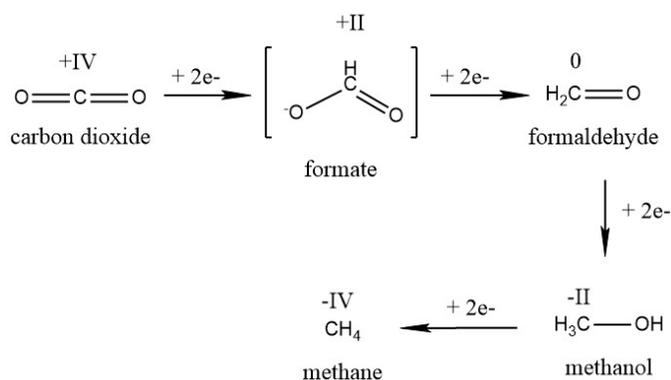


Fig. 2. Schematic pathway of carbon dioxide reduction to C1-compounds

- Loading and unloading of a carbon dioxide with hydrogen from prior water electrolysis (Hydrogen battery)
- Electrochemical reduction of carbon dioxide to formic acid or formate

Hsu et al. [9] describe the loading and unloading of a DBU-formic acid adduct at a moderate temperature of 100 °C. Pure hydrogen gas is released without carbon monoxide, which is crucial for its use in polymer electrolyte membrane fuel cells (PEM-FC).

This study however focuses on the electrochemical process as it allows a direct reduction of carbon dioxide to formic acid or formate without the need to produce hydrogen gas [10]–[12]. The reduction of carbon dioxide to C1-compounds is shown in figure 2. Formate is received by a two electron transfer.

Kopljar et al. [13] describe the electrochemical reduction of carbon dioxide in a continuous operating mode with Sn nanoparticles supported on gas diffusion electrodes. This system shows the highest reported performance indicators, with Faradaic Efficiencies over 80% and Current Densities of up to 500 mA/cm<sup>2</sup>. This due to the high overpotential towards HER and a very high active surface area within the porous carbon electrode which also avoids the problem of low CO<sub>2</sub> solubility.

The production of formate from carbon dioxide is preferred in an alkaline environment. Formate has a relatively low gravimetric hydrogen density compared to other possible hydrogen carriers. Nevertheless, it is worth to consider formate salts as they could be used for other purposes besides energy storage, e.g. as an environmental friendly de-icing agent for airports and roads [10] or used as a carbon source for microbes or synthetic enzymes to synthesize higher-value chemicals [14].

The carbon dioxide needed as a basic product could be gained from several sources. It occurs as an industrial by-product (e.g. cement and steel production) or at the combustion carbon based energy carriers (e.g. at power plants). For different approaches to capture and store carbon dioxide see [15].

Formic acid, as well as formate could be directly utilized in so called direct liquid fuel cells (DLFC) in its liquid

state without the prior release of hydrogen gas [16], [17]. Another utilization path is the use of hydrogen after dehydrogenation from formic acid in conventional PEM-FCs. The dehydrogenation of formic acid is described by several groups [18]–[26]. However, the re-electrification is not part of this study.

Hydrogen or hydrogen containing substances are versatile energy carriers which could be used for energy storage in urban environments. For example, the project "Hydrogen for the urban energy transition" investigates the possibility of a city district which is supplied by renewable energy with a central water electrolysis unit to store surplus electrical energy as hydrogen for mobile applications and re-electrification [27]. In a comparable scenario the direct electrochemical reduction of carbon dioxide to formate could be a promising alternative, as the necessity to store hydrogen gas ceases. Formate however could easily be stored over longer periods either in aqueous solution or in its solid form. The use of formate salts for hydrogen storage was already discussed in 1986 by Zaidman et al. [28] and the formate-bicarbonate cycle was identified as promising.

This study evaluates the boundary conditions and possible restriction for a seasonal energy storage in the form of formate for urban applications coupled with heat-pump demand response as described by Eicker et al. [29].

First, a test rig for the experimental study of a micro flow electrolysis cell (MFEC) is described. The MFEC in this paper is based on the formate production as the used catalyst is known to work ideal under alkaline conditions. The produced formate is considered for seasonal energy storage and as a hydrogen source for hydrogen fuel cells. Second, a theoretical background for the calculation of the formate production is given. A possible structure of a city district energy storage system based on electrochemical formate production is shown and major subsystems are explained including distribution of aqueous formate solutions. Building simulations are used to determine import framework conditions.

## II. MFEC AND TEST RIG

The choice of a suitable, commercially available reactor was based on considerations regarding the type of reactor include conceptual differences like divided/undivided cell, batch/flow reactor, three/two electrode set-up and differences in reactor design like cell volume, reactor material, flexibility of the set-up, electrode geometries/areas and such. In general a three electrode set-up with little cell volumes and the possibility to separate the cathode chamber from the anode chamber by means of a membrane is advantageous.

The stacked filter-press type design of the MicroFlowCell (see fig. 3) purchased from ElectroCell fulfills the demands best. The modular set-up makes it very versatile and adaptable. The relative big electrode area of 10 cm<sup>2</sup> and the low volume of about 5 ml allows for sufficient product concentrations even at low activities.



Fig. 3. The MicroFlowCell

The micro flow electrolysis cell (MFEC) (see fig. 3) used in this study for the electrochemical reduction of carbon dioxide to formate consists of two inner flow fields for the distribution of the anolyte and catholyte and two outer flow fields which are connected to a thermostat to control the temperature of the stack. The cathode reaction under alkaline conditions is characterized as follows:



The catholyte is composed of a 1:1 volumetric mixture of water and isopropanol (iPrOH) as hydrogen source with a KOH concentration of 1 M. The catalyst  $\text{RuCl}_2(\text{PPh}_3)_3$  (Dichloro- tris(triphenylphosphin)-ruthenium(II)) is commercially available and showed activity in transferhydrogenation reactions as well as electroreductions. However, the application in the electroreduction of  $\text{CO}_2$  is novel.

The described system is based on previous experiments in an autoclave reactor which showed the successful formation of formate under 50 bar  $\text{CO}_2$  atmosphere and at  $80^\circ\text{C}$ . The aim is to run the reaction at milder conditions (atmospheric pressure,  $\text{RT}-50^\circ\text{C}$ ) by applying a potential to drive the catalytic reaction.

This requires investigations on the electrochemical reaction engineering as well as the chemical level. In order to investigate the cathode reaction independent of the anode reaction it is possible to either use a reference electrode, that has to be placed as near as possible to the cathode surface which is challenging in the small dimensions of the flow field, or an anode reaction is chosen that has a potential of zero by definition, the hydrogen reduction. These options are currently under evaluation. The reaction path is shown in fig. 4.

A test rig to characterize the system behavior of the Micro Flow Electrolysis Cells (MFEC) was set up as shown in fig. 5. The current to maintain the electrolysis is provided by a potentiostat. A pump takes care of a continuous catholyte flow through the cell. In order to adjust different reaction temperatures, a thermostat is used to pump thermal conditioned water through the heating/cooling compartment of the cell.

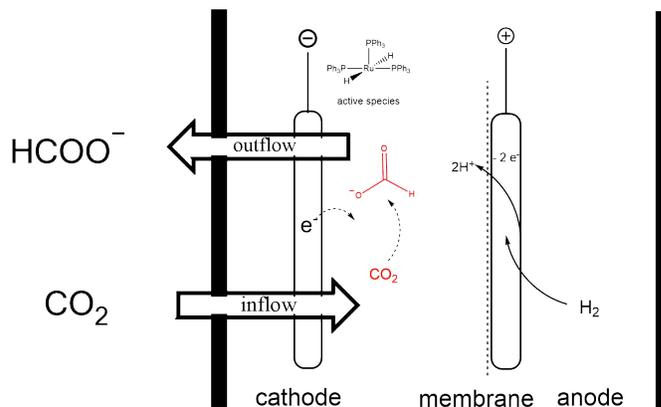


Fig. 4. MFEC reaction path

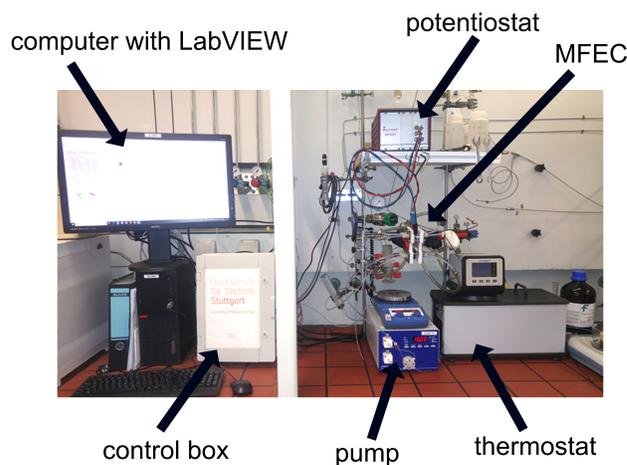


Fig. 5. Picture of the MFEC test rig

All data from sensors are matched in the control box where a real-time control system from National Instruments is built-in. The data are processed and visualized using a computer with LabVIEW software. Fig. 6 shows the sensors used to characterize the system which are summarized in table II.

Subsequently it is frequently referenced to a three molar

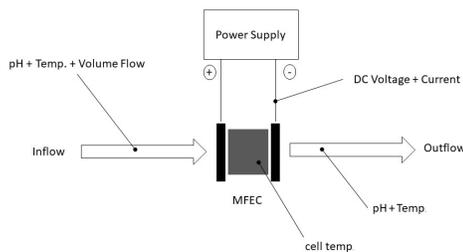


Fig. 6. Measurement variables of the MFEC test rig

TABLE II  
MEASUREMENT VARIABLES AND SENSORS

Variable	Sensor	Location
Temperature	Thermocouple type K	in-, outflow, cell surface
pH value	pH electrode with transmitter	in-, outflow
DC current	provided by potentiostat	cell electrode
DC voltage	provided by potentiostat	cell electrode
Volume flow	from pump setting	inflow

(3M) formate solution. That is due to practical reasons: An et al. [17] describe direct formate fuel cells fed by formate solutions up to 3M. As dilution is always an option, higher concentrated solutions are preferable regarding energy densities (see section IV-C). But at higher concentrations salts tend to precipitate.

The investigation of the molecular electroreduction of CO<sub>2</sub> is clearly placed in the field of fundamental research. It has to be evaluated whether molecular catalysts show the potential to be applied in technological applications of the future. These efforts are complemented by system related evaluations to clarify under which circumstances and conditions such a technology can be implemented.

### III. SIMULATION MODEL

To further investigate the system dynamics of MFECs coupled with buildings and renewable energy sources a simulation model is built. This section describes the governing equations. The specific parameters to fit the MFEC characteristics must be determined experimentally.

#### A. Electrical Model

Purpose of the electrical model is to outline the current-voltage-characteristics of the electrolysis process at any given operating point. From thermodynamics the cell voltage at standard conditions is given by:

$$E_0 = \frac{\Delta G}{zF} = \frac{\Delta H - T\Delta S}{zF} \quad (1)$$

This open circuit voltage (OCV) is the minimum voltage which must be provided to start the electrolysis process. Table III shows the OCV for water splitting and carbon dioxide reduction to formic acid.

TABLE III  
ANODE AND CATHODE CELL VOLTAGE

Electrode	Reaction	Half cell voltage
Anode	Water splitting	1.23 V @ pH0
Cathode	CO <sub>2</sub> reduction	-0.61 V @ pH7

The information of the pH-value in table III already suggest a pH-dependency of the cell potential. This dependency is described by the Nernst equation:

$$E = E_0 + \frac{RT}{zF} \cdot \ln \left( \frac{[Ox]}{[Red]} \right) \quad (2)$$

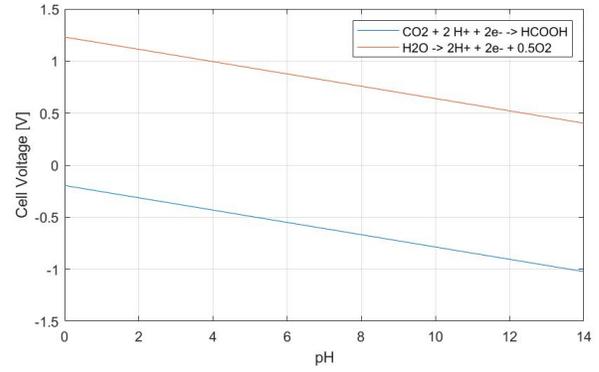


Fig. 7.

Which could be transformed regarding the proton concentration to

$$E = E_0 + \frac{RT}{zF} \cdot \ln(10^{-pH})^z \quad (3)$$

Fig. 7 shows the Pourbaix diagram of the water splitting and carbon dioxide reduction calculated with equation 3. In this case the cell potential at any identical pH-value on anode and cathode is calculated as follows:

$$E_{cell} = E_{0,cathode} - E_{0,anode} = -1.426 \text{ V} \quad (4)$$

The negative sign indicates that energy must be feed to the system to maintain the reaction. In operation the real voltage of the electrolysis will be higher due to losses. Voltage losses could be divided into:

- Activation overpotential
- Ohmic overpotential
- Mass transport overpotential

For detailed explanation and calculation of voltage losses see [30]. Finally the cell voltage is worked out with:

$$U = E_0 + U_{activation} + U_{transport} + U_{ohmic} \quad (5)$$

#### B. Substance production rate

The substance production rate is calculated with Faradays first law, which states the amount of produced substance is proportional to the amount of electrical charge flowing through the electrolyte.

$$q = n \cdot z \cdot F \leftrightarrow n = \frac{q}{zF} \quad (6)$$

With the electrical current  $I = dq/dt$  follows

$$\dot{n} = \frac{I}{zF} \quad (7)$$

#### C. Faraday efficiency

The Faraday efficiency is an important parameter to evaluate electrolysis processes as it states how much of the expended electrical energy yields in the desired product. For a liquid product it calculates as follows:

$$\eta_F = \frac{c \cdot V \cdot z \cdot F}{I \cdot t} \quad (8)$$

A low Faraday efficiency indicates unwanted side reactions.

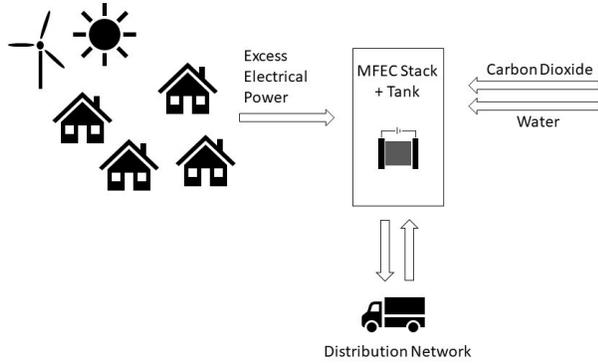


Fig. 8. Overview of formate production, storage and distribution (without re-electrification)

#### D. Thermal Model

To outline the MFECs dynamic behavior, e.g. start-up after stand-by periods or dealing high-fluctuation loads, a thermal model is implemented. The thermal characteristic of the MFEC is described by the following differential equation (with the amount of cell  $N$  and the effective heat capacity  $C_{eff}$ ):

$$(U_{cell} - U_0) \cdot I \cdot N + \dot{Q}_{heat} - \dot{Q}_{loss} - C_{eff} \cdot \frac{dT}{dt} = 0 \quad (9)$$

According to [31] the thermal losses term  $\dot{Q}_{loss}$  is determined as follows:

$$\dot{Q}_{loss} = K_v \cdot \left( \frac{T - T_{amb}}{\Delta T_0} \right)^{1+m} \quad (10)$$

$K_v$ ,  $m$  and  $C_{eff}$  must be evaluated experimentally;  $\Delta T_0 = 1K$

#### IV. FORMATE BASED CITY DISTRICT ENERGY STORAGE

Figure 8 shows a possible system integration for a formate-based energy storage system. The excess electrical energy produced by renewable energy sources is used for the electrolysis of carbon dioxide and water, releasing an aqueous formate solution. The liquid energy carrier could be stored over long periods (e.g. seasonal storage). As the existing fuel distribution infrastructure is based on liquids (tank cars etc.) a distribution network for formate is easily feasible.

The individual subsystems shown in Figure 8 are described subsequently.

##### A. Buildings and energy systems

To provide electrical load profiles suitable for this research, a white box simulation model based on a representative energy efficient residential building is utilized. The real building is situated in the town of Wüstenrot in south-west Germany and was fitted with detailed monitoring equipment, allowing the validation of the simulation model. The investigated building has a living area of  $317m^2$ , a PV system with  $13.7kWp$ , a brine/water heat pump with  $20kW$  thermal power and

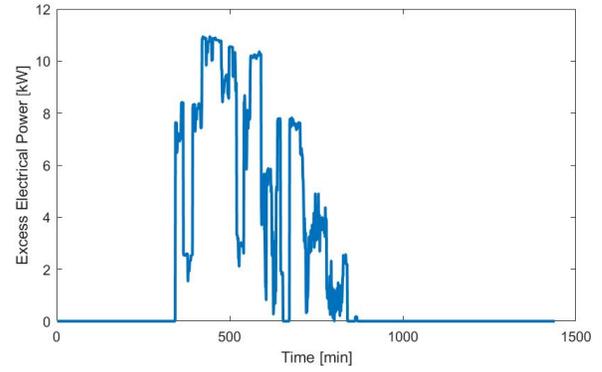


Fig. 9. Excess Energy for a representative day resulting from the building simulations

approximately  $4kW$  electrical demand and two buffer storage tanks ( $1000l$  space heating,  $300l$  DHW). User behaviour driven household electricity and DHW demand is also included. In addition, a  $5kW$  small wind turbine is added to the model, resembling a solar-wind hybrid power system with power to heat application, generating high dynamic electricity demand and production fluctuations. For this work, an annual time series of the hybrid systems excess electrical power is derived from the simulation model, to examine the formate storage potential with the aim to avoid grid infeed and stress.

The building and energy system data are summarized in table IV.

TABLE IV  
BUILDING PARAMETERS

Property	Value
Building area	$317m^2$
PV	$13.7kWp$
Heat pump thermal	$20kW$
Heat Pump electrical demand	$4kW$
Wind turbine	$5kW$

Figure 9 shows the simulation output of the excess electrical energy for one representative day. This energy could be used for the electrochemical carbon dioxide reduction. It is visible that high-fluctuations of the energy output occur, besides stand-by periods. Such load profiles from building simulation outputs could be used to investigate the MFEC behavior under such circumstances at the test rig.

##### B. Electrolysis Unit

The amount of cells must be adjusted to fit input power by connecting cells in series (stacks) and several stacks in parallel. According to Kirchhoffs law the sum of voltages in a closed loop is zero

$$\sum_{k=1}^n U_k = 0 \quad (11)$$

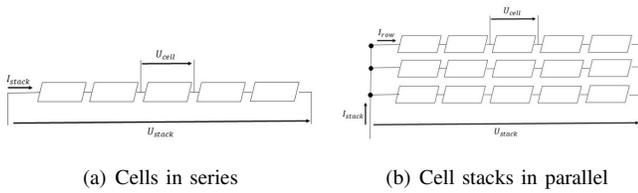


Fig. 10. Wiring of MFECs

If the potential for all connected cells is assumed to be equal the sum could be simplified by

$$N_{row} \cdot U_{cell} - U_{stack} = 0 \quad (12)$$

The current  $I_{total}$  is valid for the entire electrolysis unit. It is calculated as:

$$I_{total} = \frac{P_{max}}{U_{stack}} \quad (13)$$

Only serial cell connection includes the risk of a system failure if one cell is not working correctly. To increase the system reliability multiple stacks of cells could be connected in parallel. In this case a cell failure would not lead to an immediate system shutdown. Additionally, in this way the current could be adjusted, as the input current equally splits to the number of stacks connected.

$$I_{stack} = \frac{I_{total}}{N_{stack}} \quad (14)$$

The state-of-the-art specification for the cell area in PEM-Electrolyzer cells is less than  $300 \text{ cm}^2$  [30]. For this study a possible active cell area of  $100 \text{ cm}^2$  is assumed. With the current density given at an optimal operating point the maximum input current calculates as:

$$I_{cell,max} = i_{max} \cdot A \quad (15)$$

The number of cells must be determined and connected in a way that the maximum current input is not exceeded at any point. Figure 10 shows the wiring of cells to stacks and of multiple stacks in parallel.

Taking the maximal occurring input power given in figure 9 of  $10941 \text{ W}$  and an estimated operation voltage of  $2.2 \text{ V}$  at  $10 \text{ mA cm}^{-2}$ , the volume flow of potassium formate solution could be approximated (with equation 8 and 13 and parameters given in table V):

$$\dot{V} = \frac{\eta_F \cdot I_{cell}}{c \cdot z \cdot F} \quad (16)$$

TABLE V  
PARAMETERS FOR THE CALCULATION OF THE FORMATE VOLUME FLOW

Parameter	Symbol	Value	Reference
Desired concentration	$c$	$3 \text{ mol L}^{-1}$	-
Faraday efficiency	$\eta_F$	0.45	[21]
Cell voltage	$U_{cell}$	$2.2 \text{ V}$	[21]
Current density	$i$	$10 \text{ mA cm}^{-2}$	[21]
Cell area	$A$	$100 \text{ cm}^2$	assumption
Max Power input	$P_{max}$	$10941 \text{ W}$	-

This results in a theoretical maximal volume flow of a  $3\text{M}$  potassium formate solution of  $\dot{V}_{formate,max} = 7.77 \times 10^{-7} \text{ L s}^{-1}$  per cell.

Nevertheless this would result in a very high amount of needed cells. A stack of 50 cells would result in a stack voltage of  $U_{stack} = 110 \text{ V}$  (equation 12) and an overall current of  $I_{total} = 99.46 \text{ A}$  (equation 13). The current density of  $10 \text{ mA cm}^{-2}$  at the operating point and the assumed cell area of  $100 \text{ cm}^2$  leads to a cell current of  $I_{cell} = 1 \text{ A}$ . Hence, theoretically about 100 stacks of 50 cells must be connected in parallel to fit the maximum power input of  $10941 \text{ W}$  (equation 14).

### C. Tank and energy density aspects

According to Sterner/Stadler [32] the amount of surplus electrical energy which could be stored calculates as follows:

$$W_{in} = \int_{t_1}^{t_2} P_{in}(t) \cdot dt \quad (17)$$

The tank size for formate storage in aqueous solution form could be calculated taking the overall efficiency of the MFEC system  $\eta_{total}$ , the HHV of hydrogen and the formate concentration into account.

$$V_{tank} = \frac{2 \cdot W_{in} \cdot \eta_{total}}{HHV_{H_2} \cdot c} \quad (18)$$

There are no restriction concerning the wall material for a tank filled with formate solution.

Besides the possibility to store formate salts solved in aqueous solutions it is conceivable to store them in its solid form, which would increase the gravimetric energy density with regard to the hydrogen amount.

The gravimetric energy density is calculated as follows<sup>1</sup>. For solid products:

$$w_{grav} = \frac{\nu \cdot HHV_{H_2}}{M} \quad (19)$$

For aqueous solutions, with the molarity  $b$  [ $\text{mol L}^{-1}$ ]:

$$w_{grav,aq} = \frac{b \cdot \nu \cdot HHV_{H_2}}{b \cdot M + \rho_{H_2O}} \quad (20)$$

The calculated gravimetric energy density for solid potassium formate as well as for aqueous formate solutions at different concentrations are shown in table VI and table VII.

TABLE VI  
GRAVIMETRIC ENERGY DENSITIES OF SOLID POTASSIUM FORMATE SALT

Substance	Molar weight	Energy density
$\text{KHCO}_2$	$83.98 \times 10^{-3} \text{ kg mol}^{-1}$	$1.7 \times 10^3 \text{ kJ kg}^{-1}$

All values in table VII are calculated with equation 20 and  $\rho_{H_2O} = 1 \text{ kg L}^{-1}$ .

The calculated gravimetric energy densities show that when stored as a solid about five times higher energy densities are

<sup>1</sup> $\nu = 0.5$  as 1 mole of formate yields half a mole hydrogen

TABLE VII  
GRAVIMETRIC ENERGY DENSITIES OF AQUEOUS POTASSIUM FORMATE SOLUTIONS

Substance	Molarity	Energy density
$\text{KHCO}_{2aq}$	$1 \text{ mol L}^{-1}$	$0.132 \times 10^3 \text{ kJ kg}^{-1}$
$\text{KHCO}_{2aq}$	$3 \text{ mol L}^{-1}$	$0.343 \times 10^3 \text{ kJ kg}^{-1}$
$\text{KHCO}_{2aq}$	$5 \text{ mol L}^{-1}$	$0.504 \times 10^3 \text{ kJ kg}^{-1}$

achieved compared to a 3M aqueous solution. Storing formate salts in its solid form is also offering the opportunity to enrich liquid solutions and any wanted concentration depending on the desired application.

To precipitate the salt from its solvent it is necessary to cool down the solution under the solubility equilibrium. At  $-20^\circ\text{C}$  still  $31.8 \text{ mol kg}^{-1}$  of potassium formate is solvable<sup>2</sup>. This means that very low temperatures are needed to actually precipitate the salts. Other formate salt show lower solubility. Only  $4.34 \text{ mol kg}^{-1}$  of sodium formate is solvable in water at  $-20^\circ\text{C}$ . Yet there are formate salts with very low solubility, e.g. nickel formate ( $\text{Ni}(\text{HCO}_2)_2$ ) with only  $0.137 \text{ mol kg}^{-1}$  at room temperature. Nevertheless, considering solid  $\text{K}(\text{HCO}_2)$  as energy storage substances cooling energy has to be provided.

#### D. Distribution

Liquid renewable energy carriers allow to use already existing infrastructure for liquid fossil energy carriers. A distribution network enables the balancing of stored energy between different locations, for example between windy and less windy locations, without the need of additional high voltage links.

Subsequent it is determined how much equivalent energy could be stored in an average tank car for rail transportation of formate solutions.

TABLE VIII  
PARAMETERS FOR AN AVERAGE TANK CAR

Property	Symbol	Value
Tank car volume	$V_{tank}$	$70 \text{ m}^3$
Maximal net cargo load	$m_{cargo}$	$67.2 \text{ t}$
Moles $\text{H}_2$ per mole formate		$0.5$
Molar weight of potassium formate	$M$	$0.084 \text{ kg mol}^{-1}$

As the density of formate solutions are always higher than that of pure water, the formate load in this case is limited by the weight rather than the volume (equation 21).

$$V_{max} = \frac{m_{cargo}}{\rho} = \frac{67\,200 \text{ kg}}{997 \text{ kg m}^{-3}} = 67.4 \text{ m}^3 < V_{tank} \quad (21)$$

With values from table VII follows the energy equivalent stored in a tank car for potassium formate aqueous solutions.

<sup>2</sup>IUPAC-NIST Solubility DB, DOI: <http://dx.doi.org/10.18434/T4QC79>

TABLE IX

Substance	Molarity	Energy equivalent in tank car
$\text{KHCO}_{2aq}$	$1 \text{ mol L}^{-1}$	2464 kW h
$\text{KHCO}_{2aq}$	$3 \text{ mol L}^{-1}$	6402 kW h
$\text{KHCO}_{2aq}$	$5 \text{ mol L}^{-1}$	9408 kW h

## V. CONCLUSION

In this paper a possible decentralized city district hydrogen storage system is described based on the reduction of carbon dioxide to formate. Such a system is offering great flexibility compared to a state-of-the-art hydrogen storage gas storage. The liquid state of formate solutions allow easy long-term storage and the use of existing transportation infrastructure (tank cars etc.). The low gravimetric energy density of formate is balanced by advantages such as non-toxicity, low safety requirements and the possibility of formate utilization for different purposes such as de-icing agents. Nevertheless the low energy density seems to limit formate for its use in stationary applications.

As described in this paper it is intended to execute the carbon dioxide reduction electrochemically in micro flow electrolysis cells (MFEC). This approach allows a formate production without the need to handle gaseous hydrogen. The development of a test rig for detailed experiments is shown.

The general simulation model is optimized to fit the MFEC characteristics with experimental data. A thermal model will be included. Dynamic system simulations will give a detailed impression of the system behavior including stand-by phases and high load fluctuations occurring when the electrolysis process is driven by solar and wind energy. Formic acid salts could also be stored in its solid state increasing the gravimetric energy density. New application paths arise for saline energy carriers as concentrations of solutions could be adapted for the specific purpose of the salt (Direct Liquid Fuel Cell, dehydrogenation, industrial application). In further studies the technical conditions to precipitate formic acid salts of the solution are evaluated.

To answer the initial question if formate is suitable for urban seasonal energy storage, it could be summarized that formate or formic acid are promising options for future energy carriers. Nevertheless a lot of research effort must be carried out. As it turns out, for practical applications of an electrochemical carbon dioxide reduction the overall amount of cells must be decreased. This could be achieved by the following improvements:

- Increase of the cell area
- Increase of the Faraday efficiency with efficient and high-selective catalysts
- Increase of the operating cell current density

Some system integration aspects of carbon dioxide electrolysis units must be evaluated as well, such as system assembly (with

subsystems such as pumps), electrical and hydraulic interfaces, as well as operating modes and control algorithms.

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