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Studies on Fe/Fe Redox Flow Batteries with Recombination Cell

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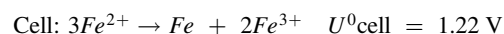
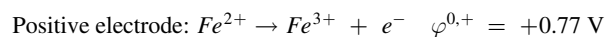
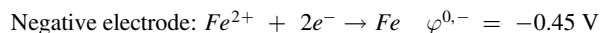
Different Fe/Fe redox flow batteries were constructed and investigated. The aim of the work was to assess the feasibility of Fe/Fe redox flow batteries as potentially inexpensive candidates for stationary energy storage for renewable energy. A recombination cell was developed and integrated into the battery. The recombination cell should prevent irreversible loss of capacity caused by hydrogen generation. Furthermore, electrolyte regeneration experiments with external hydrogen were conducted to reverse irreversible losses. With the battery and recombination cell up to 100 two-hour charge and discharge cycles were carried out and different materials were investigated. Different substrate materials for iron deposition were compared and different microporous and ion exchange membranes were used. A kynol fabric achieved the best performance and all membranes investigated showed potential applications. An optimized battery achieved up to 70% energy efficiency at 12.5 mA cm⁻² and max. 47 mW cm⁻² power density at 75 mA cm⁻².

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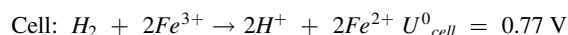
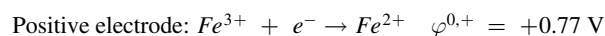
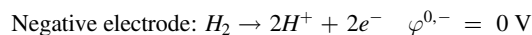


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Due to fluctuating energy production and the significant increase in renewable energy producers such as wind power and photovoltaics, the need for stationary energy storage systems is increasing.^{1,2} Electrochemical energy storage systems have the advantage of decentralized use and modular scaling with potentially low lifetime costs. The most common technologies currently in use are lead/acid (LAB), lithium-ion (LIB), sodium/sulphur and vanadium redox flow batteries (VRFB).³ All these technologies have been or are currently being significantly extended in the MW/MWh range worldwide, although lead/acid batteries are being replaced. A disadvantage of lithium-ion batteries is the partly questionable raw material procurement⁴ and recycling,⁵ as well as the service life of the batteries to be achieved. Lithium-ion batteries in very large-scale devices also present a safety concern. Compared to conventional batteries, redox flow batteries (RFB) have the advantage that power and energy can be scaled separately and can therefore be better adapted to the respective requirements.⁶ Vanadium redox flow batteries (VRFB) offer the possibility of potentially easy recycling by reusing used vanadium solution, but the price of vanadium has fluctuated significantly in the past.⁷ High costs for vanadium as a raw material for the energy storage medium have a direct impact on investment costs and can prevent successful commercialisation. In addition, the maximum temperature limitation of VRFBs for use in very warm and sunny regions is an obstacle, since the effort for heat management directly affects the investment costs and additionally influences the efficiency and thus the specific storage costs. For these and other reasons, almost countless alternative redox flow batteries based on inorganic and organic redox pairs and electrolytes have been investigated in recent years,^{8,9,10} Especially aqueous organic redox pairs have attracted a lot of attention in recent years. The motivation for this was mostly a reduction of investment costs by using active materials that are as inexpensive as possible. The iron/iron redox flow battery is also a representative with extremely inexpensive active materials and was first investigated by Hruska and Savinell in 1981.¹¹ The Fe/Fe-RFB uses iron as the sole active material in the three different oxidation states 0, +2, and +3. During the charging process, metallic iron is deposited from an iron(II) solution at the negative electrode and is oxidized to soluble iron(III) at the positive electrode (see also Fig. 1):



A major challenge for this type of battery is the negative deposition potential for iron and the relatively high kinetics of hydrogen generation at iron electrodes. The kinetics of hydrogen formation is pH-dependent and slows down with increasing pH values, which favors iron deposition. The pH value of the negative electrolyte solution increases due to the hydrogen formation, especially at the electrode. Above a roughly neutral pH value, sparingly soluble iron(II) hydroxide is formed and is removed from the battery, causing a loss of capacity because of electrochemical inactivity. Furthermore, precipitates are formed on electrodes and in the fluidic system, which can lead to an increase in internal resistance or pressure loss and thus to battery failure. In connection with this, past work has dealt with an optimized electrolyte composition.^{12,13} This includes conducting salts, buffers^{14,15} and metal ions to increase the overvoltage for hydrogen generation but also different organic ligands.^{16,17,18} The stabilization of the pH value at the electrode is an important aspect for achieving high performance batteries with high efficiencies. However, there will always be a non-negligible amount of hydrogen, which is associated with a continuous loss of capacity and must be prevented or compensated for. One possibility is the electrochemical reversal of the side reactions in a separate electrochemical cell.^{19,20,21} The hydrogen produced is oxidized on a catalyst layer and iron(III) ions from the positive electrolyte are reduced to iron(II) ions:



The difference between the standard potentials is 0.77 V. The cell reaction almost completely reverses the secondary reaction, with the exception that in the overall balance protons are transported from the negative electrolyte to the positive electrolyte and the pH of the positive electrolyte decreases while that of the negative electrolyte increases. In addition, there is a loss of energy, but theoretically this can be partially used.

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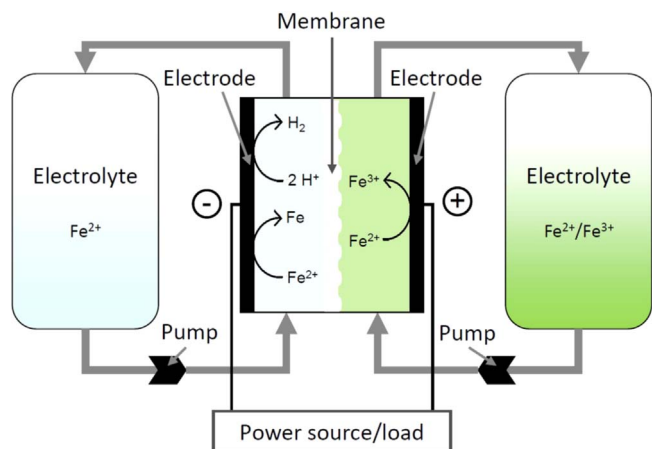


Figure 1. General schematics of an iron/iron redox flow battery—Reactions are in direction of charge process.

Within the scope of this work we were mainly interested in the basic properties of Fe/Fe-RFBs and whether they could have the potential for commercial application. For this purpose, we were particularly interested in the problem of the lifetime of energy storage media in connection with recombination and regeneration possibilities. Furthermore, different substrates and membranes were investigated for their applicability in Fe/Fe-RFBs.

Experimental

For battery tests, a test stand was set up as shown schematically in Fig. 2 and as photograph in Fig. 3. The test stand consisted of an Fe/Fe-RFB cell, a recombination cell, two reservoirs for the energy storage medium, two pumps, a potentiostat (Reference 3000, Gamry, USA) and a benchtop multimeter. The supply of the media to the different cells was carried out in such a way that gaseous hydrogen from the head space of the negative storage tank could reach the negative half-cell of the recombination cell and the output of the positive energy storage medium of the Fe/Fe-RFB cell ($\text{Fe}^{3+}/\text{Fe}^{2+}$) was connected to the input of the positive half-cell of the recombination cell. The electrolyte was returned to the storage tank after passing the recombination cell. The outlet connection of the hydrogen side of the recombination cell was closed by a 100 mm high water column. The battery cell was electrically connected to the potentiostat. The recombination cell was directly connected to the current measurement of a benchtop multimeter.

The battery cell consisted of two half-cells with an active area of 40 cm^2 (see Fig. 4). The positive half-cell consisted of a flow frame (f) in which a glassy carbon plate (HTW High Temperature Materials, Germany) with a thickness of 3 mm was embedded. A graphite felt (GFA 5, SGL-Carbon, Germany) was placed in the flow frame to increase the electrochemical surface area. The graphite felt was thermally treated for 1 h at a temperature of 400°C for hydrophilization. The negative half-cell also consisted of a flow frame (f) made of polyvinyl chloride (PVC) with an embedded glassy carbon plate. The gap between frame and glassy carbon plate has been sealed with conventional silicone sealant. The flow frame had a cavity with a thickness of 3.5 mm. Various carbon fabrics or papers were placed in this cavity as substrate (j) for iron deposition. To create a cavity for iron deposition, a 3D printed spacer was also placed in the cavity. The maximum possible distance to the membrane was thus approx. 3.3–3.4 mm depending on the substrate used. The half-cells were separated by a membrane (h). Four different membranes were tested during the experiments. A cation exchange membrane (NAFION 115), an anion exchange membrane (Fumasep FAP-450, Fumatech GmbH, Germany), a microporous separator (BH-Consulting, Australia) and another microporous separator (SF-601, Asahi-Kasei, Japan). If not mentioned otherwise, the anion exchange membrane was used.

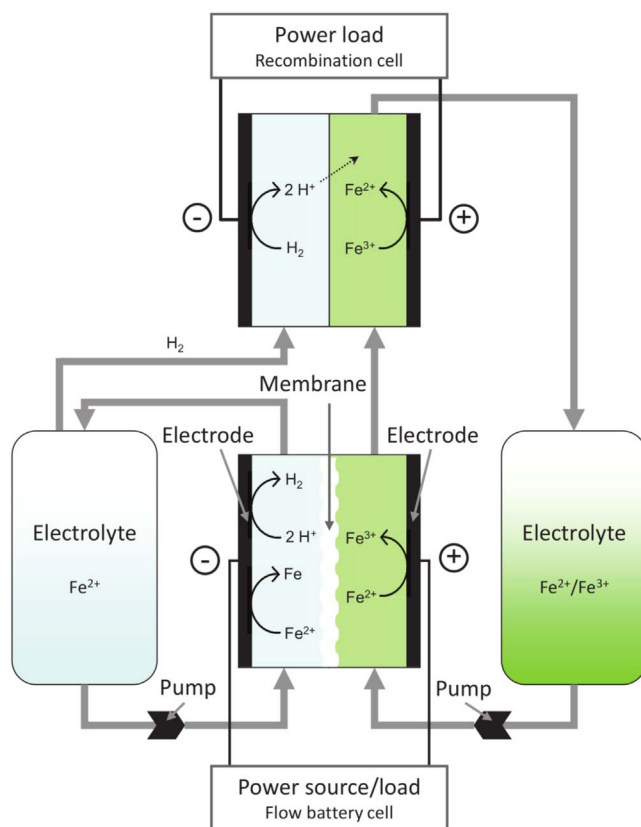


Figure 2. Schematics of an iron/iron redox flow battery with integrated recombination cell—Reactions are in direction of charge process.

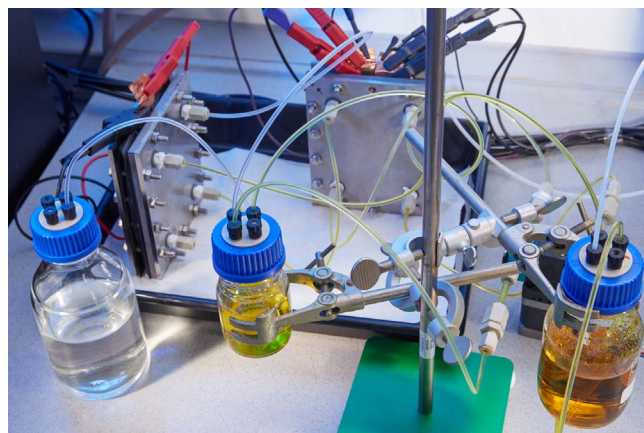


Figure 3. Picture of an iron/iron redox flow battery laboratory setup with recombination cell.

Thin copper sheets were used as current collectors. To reduce contact resistance, a carbon paper (Toray TP 30, Quintech GmbH, Germany) was placed between copper and graphite plate. Flat gaskets (c) were placed at various points to ensure tightness. The two half-cells were finally held together by two metal plates, one of which contained holes for the media inlets and outlets. An insulation plate (b) was used for electrical insulation.

As shown schematically in Fig. 5, a recombination cell was built and integrated into the battery as described above. The recombination cell consisted of two half-cells separated by a one-sided catalyst coated membrane (CCM) (NAFION 115, 1 mg cm^{-2} Pt/C, Baltic Fuel Cells, Germany). The side with the catalyst layer was the negative half-cell. The positive half-cell consisted of a glassy carbon foam as electrode (ERG Aerospace, USA), which was placed in a

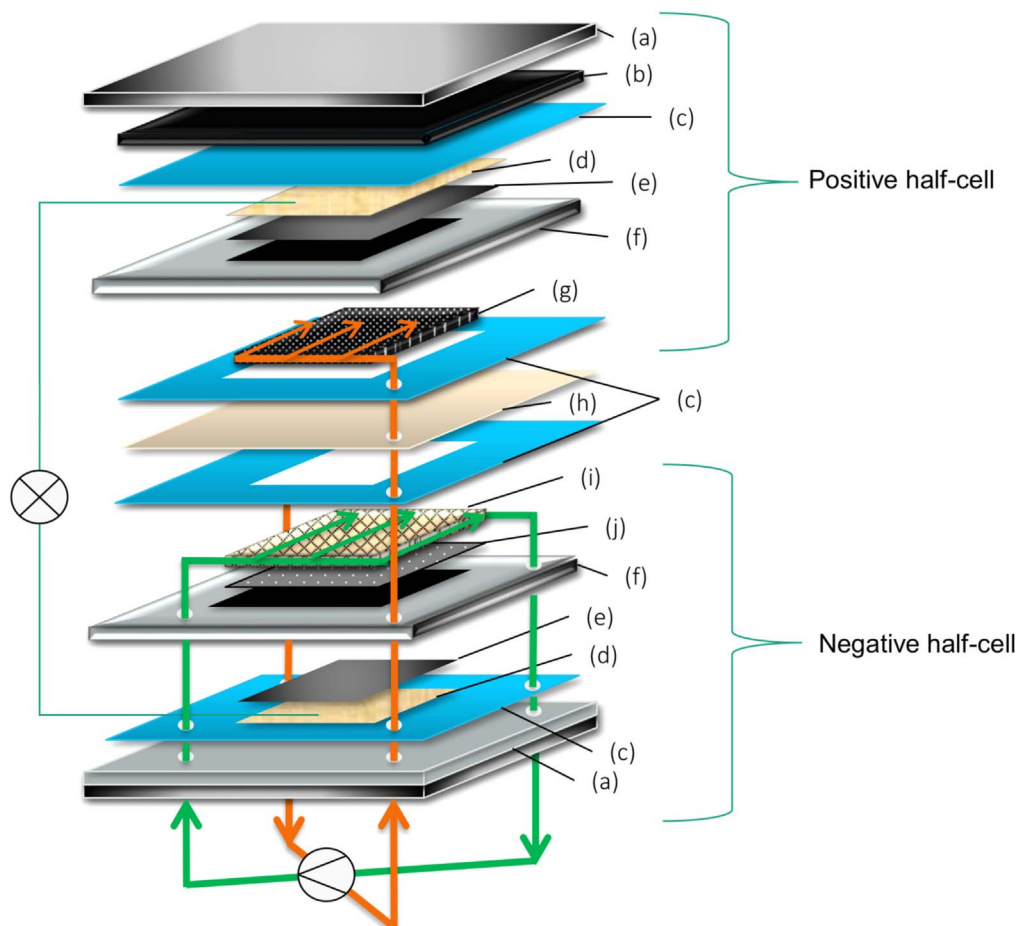


Figure 4. Schematics of an iron/iron flow cell, (a) end plate, (b) isolation plate, (c) gasket, (d) copper current collector, (e) carbon paper, (f) flow frame with graphite plate, (g) carbon substrate, (h) membrane, (i) spacer.

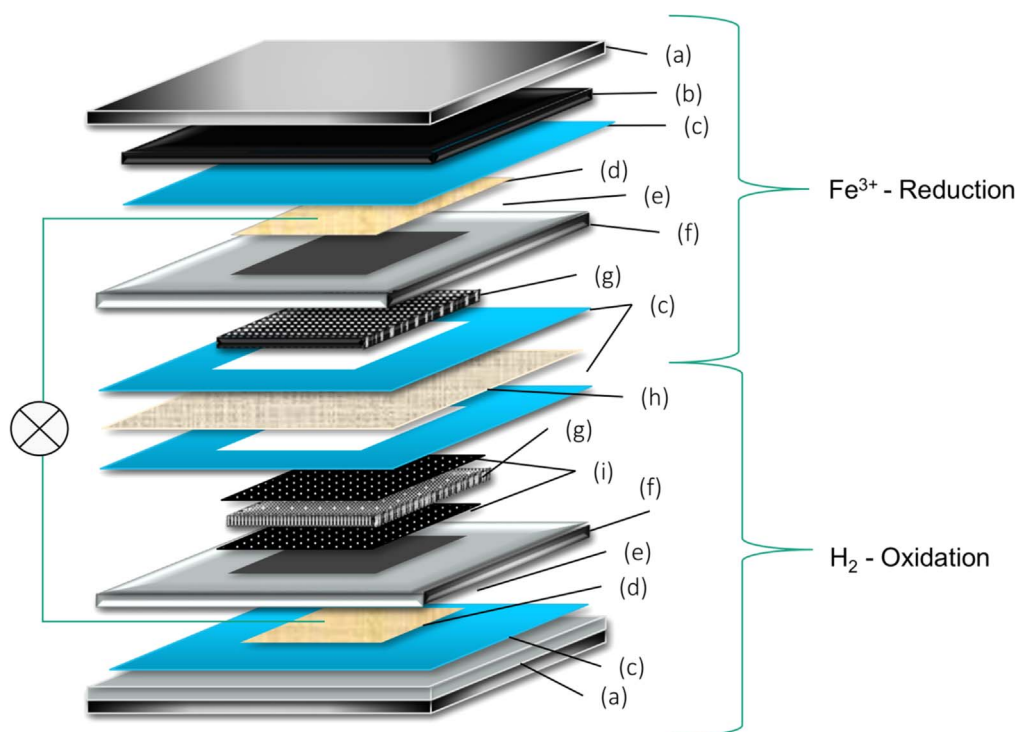


Figure 5. Schematics of an hydrogen/iron recombination cell, (a) end plate, (b) isolation plate, (c) gasket, (d) copper current collector, (e) Toray paper; (f) flow frame with graphite plate, (g) glassy carbon foam; (h) catalyst coated membrane (CCM); (i) Toray paper.

flow frame (f). A glassy carbon plate (HTW high temperature materials, Germany) was embedded in the flow frame. Thin copper sheet (d) was used as a current collector, on which Toray paper (e) was laid to reduce contact resistance. The negative half-cell again consisted of a glassy carbon electrode (g), which was placed between two Toray papers (i) in a flow frame (f) with embedded glassy carbon plate. Again a thin copper plate served as current collector. The cell was sealed by different flat gaskets (c). The components were held together by two steel plates (a), one of which had the media feed-throughs.

A solution of 1 M FeCl_2 , 2 M NH_4Cl and 0.2 M HCl with a pH < 0 served as energy storage medium. The solution was initially used for both half-cells. The volume of the negative electrolyte was either 30 or 60 ml. The volume of the positive electrolyte was either 60 ml or 120 ml. The theoretical maximum capacity was 1.62 Ah (30 ml/60 ml) or 3.24 Ah with double the electrolyte volume. The positive electrolyte was continuously purged with nitrogen.

Charging and discharging tests were carried out to investigate the properties of different cell materials, current densities and charging and discharging parameters. Between the tests, a new cell was set up, the fluidic system was cleaned and new portion of electrolyte was used. For a new cell a new felt was always used for the positive electrode, a new substrate for the negative electrode and a new membrane. The charge and discharge experiments were carried out galvanostatically with a constant current. To check the ohmic resistance of the battery cell, impedance measurements were taken before each measurement on a newly constructed cell and the ohmic resistance was determined by reading the intercept on the X-axis at high frequencies in the Nyquist plot.

Electrolyte regeneration was performed using the same setup shown in Fig. 2. The aim of the study of the electrolyte regeneration was to verify the regeneration of capacity and composition of the electrolyte by Hydrogen loss to the atmosphere. Regeneration was performed with externally supplied hydrogen after the battery cell was completely discharged and the positive electrolyte was pumped into the negative electrolyte circuit and then back into the positive electrolyte circuit. The electric current of the recombination cell was measured by a benchtop multimeter and regeneration was continued until the electric current density was less than 0.25 mA cm^{-2} . The content of Fe^{2+} and Fe^{3+} was determined by potentiometric titration. Iron content measurements were made on a freshly prepared Fe(II) solution, the solution before regeneration and the solution after regeneration. All experiments were carried out at room temperature. All experiments were carried out with recombination cell except the comparison in Fig. 6 at the beginning of the results.

Results and Discussion

Figure 6a shows an example of voltages of an Fe/Fe-RFB without recombination cell during the charge and discharge. The standard potential difference is 1.22 V. The overvoltages to this value were about 150 mV during charging (at SOC 50) and 350 mV during discharging. It is known that the positive redox reactions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ are electrochemically reversible and therefore fast.^{22,23} Thus, iron dissolution was much slower than iron deposition and a limiting factor for battery efficiency. The area specific resistance (ASR) of the battery cell was 5.4 Ohm cm^2 and thus comparatively high. The ohmic resistances of all further experiments were in the range between 90–140 mOhm and thus varied quite strongly. In this cell, the loss due to the ohmic resistance was 136 mV alone during charging and discharging and was thus also a significant factor in the efficiency losses.

The cell voltage polarized to a value of approx. 1.6 V at the beginning of the charging process, decreased slightly and increased continuously until the maximum charging time of 1 h was reached or the final charging voltage of 1.9 V was reached. This behaviour is typical for metal deposition on carbon electrodes, where the kinetics of iron deposition on carbon is lower than on the deposited metal itself. Only the first two charging processes were limited by time.

Table I. Capacities of a charge and discharge experiment with an Fe/Fe redox flow battery without recombination cell (1 M FeCl_2 , 2 M NH_4Cl , 0.2 M HCl , $i = 25 \text{ mA cm}^{-2}$, $t_{\text{charge, max}} = 1 \text{ h}$).

Cycle Nr.	$C_{\text{Discharge}}/\text{Ah}$	$C_{\text{Charge}}/\text{Ah}$	$C_{\text{Discharge}}/C_{\text{Charge}}$
1	0.63	1	0.63
2	0.84	1	0.84
3	0.92	0.99	0.93
4	0.84	0.92	0.91
5	0.77	0.84	0.92

The following four charging processes were terminated by concentration depletion and reaching the final charging voltage. Especially during charging, a significant gas development was visible in the negative half-cell. During discharging, the cell voltage dropped to a value of approx. 0.88 V at the beginning of the first discharging process and then decreased in the further course of the charging process until the final discharge voltage of 0 V was reached due to concentration depletion.

The first discharge process achieved a discharge capacity of 0.63 Ah and thus only 63% of the theoretical value of 1 Ah. In the subsequent discharging processes, the third discharging process had the absolute highest value with 0.92 Ah. During all further discharges the capacity was continuously reduced, but the capacity utilization increased significantly to a value of 92%–93% (see Table I). This capacity behavior can be explained on the one hand by the more favorable deposition of iron due to an increase in the pH value of the negative electrolyte as a result of hydrogen loss, and on the other hand by the loss of capacity caused by the formation of hydrogen as a side reaction, which led to an irreversible oxidation of Fe^{2+} at the positive electrode. In the first cycle the pH value is too low to be able to deposit iron with a high capacity utilization. A large proportion (37%, neglecting other side reactions) was converted to hydrogen and the irreversible oxidation of Fe^{2+} . As the process progressed, the battery reached an optimum pH value for iron deposition, but had already lost a lot of capacity before and continued to lose capacity due to hydrogen formation. The difference in the discharge capacities of the 4th and 5th cycle corresponded to 70 mAh and, if only hydrogen generation was attributed to the battery, only 26 ml hydrogen loss.

Due to the strong irreversible loss of capacity and the danger of the formation of poorly soluble iron hydroxides, investigations were carried out with a recombination cell. Figure 6b shows the capacities of several charge and discharge experiments with and without recombination cell. Without the use of a recombination cell, the discharge capacity dropped to a value of 0.1 Ah within 40 cycles. The batteries with recombination cell achieved a significantly lower capacity depression by recombination of the hydrogen produced with the Fe^{3+} ions of the positive half-cell. The batteries without recombination cell only had a discharge capacity of about 0.1 Ah (10%) after 50 cycles. The batteries with recombination cells had a discharge capacity of 0.56 Ah (56%) after 50 cycles, or 0.41 Ah (41%) after 100 cycles. The decrease in capacity was still significant and dramatic for a permanent use as an energy storage device, so further investigations into its cause were conducted. The difference in discharge capacity between the 45th and 50th cycle was only 40 mAh or 17 ml hydrogen, with only 3.4 ml hydrogen loss per cycle. It was plausible that an irreversible loss of hydrogen was caused by the laboratory setup. However, other side reactions like loss of deposited iron due to poor adhesion on the electrode could not be excluded. To further investigate this behaviour, regeneration experiments with external hydrogen were carried out.

Figure 7 shows the capacities of an Fe/Fe-RFB and a recombination cell during 46 charge and discharge cycles. The charging capacity was 3.6 Ah at the beginning and decreased significantly to about 2.5 Ah in the 21st cycle. Afterwards the electrolyte was regenerated with external hydrogen. Due to side reactions the charge

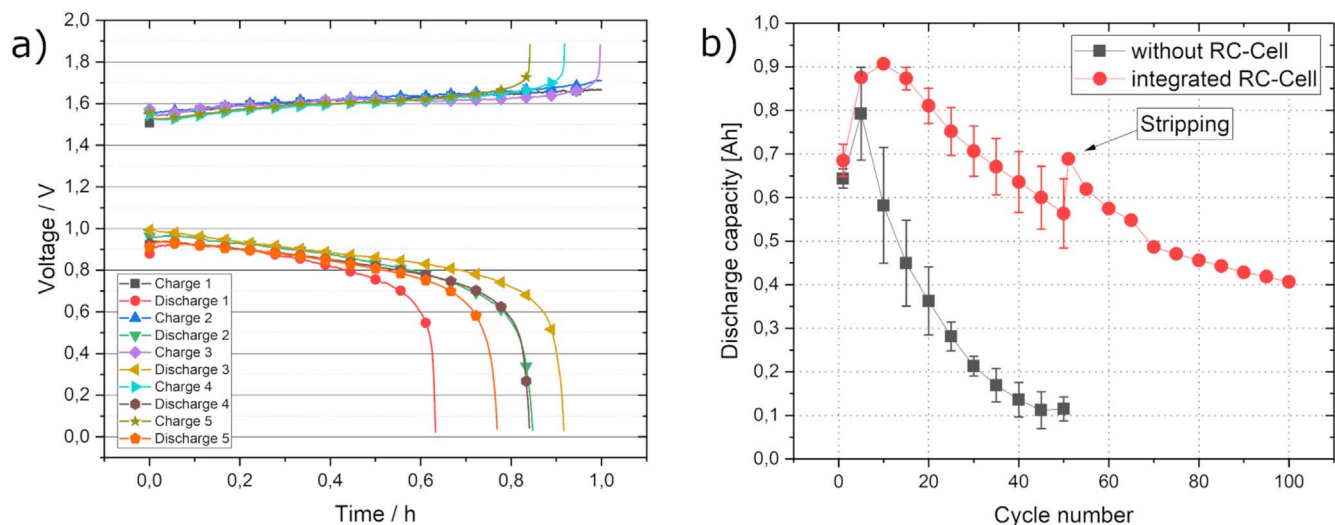


Figure 6. (a) Voltage during charge and discharge of a Fe/Fe-redox flow battery without a recombination cell (1 M FeCl_2 , 2 M NH_4Cl , 0.2 M HCl , $i = 25 \text{ mA cm}^{-2}$, $t_{\text{charge, max}} = 1 \text{ h}$); (b) Capacity of a Fe/Fe Redox Flow Battery with and without a Fe/H_2 recombination cell (0.2 M HCl , 25 mA cm^{-2} , $t_{\text{charge, max}} = 1 \text{ h}$, $U_{\text{charge, max}} = 1.9 \text{ V}$).

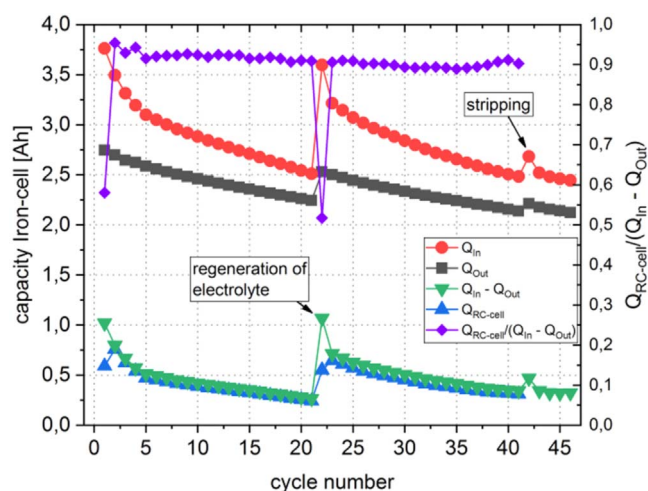


Figure 7. Capacities of an Fe/Fe redox flow battery (Q) and capacities of a recombination cell (Q_{RC}) (60/120 ml electrolyte) before and after electrolyte regeneration with external hydrogen.

capacity was always significantly higher than the discharge capacity. Side reactions include diffusion of ions through the membrane and hydrogen formation. The differences in the charging and discharging capacities (see $Q_{\text{in}} - Q_{\text{out}}$) initially had a significant drop until the 5th cycle and then decreased more or less constantly to about 0.25 Ah. As mentioned above, the pH value of the negative electrolyte was too low at the beginning and caused a high proportion of hydrogen production. By shifting the pH to more positive values, the proportion of hydrogen loss was reduced and with it the difference in charging and discharging capacities. Theoretically, it was expected that the difference would not decrease linearly, but would change to a plateau with a constant value. The reason for this assumption is the increase in the diffusion of protons from the positive half-cell space to the negative one through the membrane due to proton pumping with the help of the recombination cell. Consumption of protons at the negative electrode and back diffusion should if possible reach a constant value and bring the cell into dynamic equilibrium. The approach to such an equilibrium was not observed during the first 21 cycles, but after regeneration such a tendency was observed.

However, it should also be noted that there were possibilities for a continuous non-reversible hydrogen loss out of the system. With the exception of the first value, the conversion capacities of the recombination cell during regeneration ($Q_{\text{RC-cell}}$) decreased continuously to approx. 243 mAh in the 21st cycle. The first value was probably lower than the others because the system volume was first filled with hydrogen and could not be recombined. Roughly estimated, the system volume should still be 50–100 ml and thus contribute to a large irreversible loss of capacity. With the exception of the first cycle (58%), the recombination efficiencies ($Q_{\text{RC-cell}}/(Q_{\text{in}} - Q_{\text{out}})$) were over 90%. On the one hand, the value was thus pleasingly high, and on the other hand 10% of the losses were not regenerated by the recombination cell. In the 21st cycle, these 10% losses amounted to only 24 mAh or 10 ml hydrogen, assuming hydrogen loss as the only irreversible reaction. Considering the laboratory setup it seemed plausible that 10 ml hydrogen could be irreversibly lost during a cycle of several hours. The 24 mAh loss also matched well with the difference of 18 mAh loss between the 21st discharge capacity and the 20th discharge capacity.

After the 21st discharge cycle the battery was completely discharged at a voltage of 0 V and the positive electrolyte was pumped into the negative electrolyte circuit, all the mixed electrolyte was pumped into the positive half-cell and external hydrogen was passed through the recombination cell until there was hardly any current left. Figure 8 shows the resulting change in the mixed electrolyte. The color changed from a cloudy orange solution to a clear green solution with orange solids, which also completely dissolved over time. During regeneration, the pH of the solution was lowered and Fe^{3+} ions were reduced to Fe^{2+} . Due to the redox potential ratios, the regeneration should stop on its own when all Fe^{3+} has been reduced, which means that, unlike other regeneration processes for vanadium RFBs,⁷ the progress of the regeneration can be followed with a simple current measurement.

After regeneration, the pH value, which was finally lowered again, resulted in a similar behaviour of the capacity curves as with a freshly used Fe^{2+} solution. Titration of the regenerated electrolyte solution showed a 100% Fe^{2+} content in the solution. This was 4% more than the freshly prepared solution. However, the first discharge capacity was 2.53 Ah instead of 2.74 Ah in the first cycle. The difference could be explained by the fact that before regeneration, the positive electrolyte was first pumped into the negative half-cell to dissolve any iron deposits and then pumped back again. A portion of Fe^{3+} ions could thus remain in the negative half-cell and in the fluid system and was not available for regeneration. Based on the results

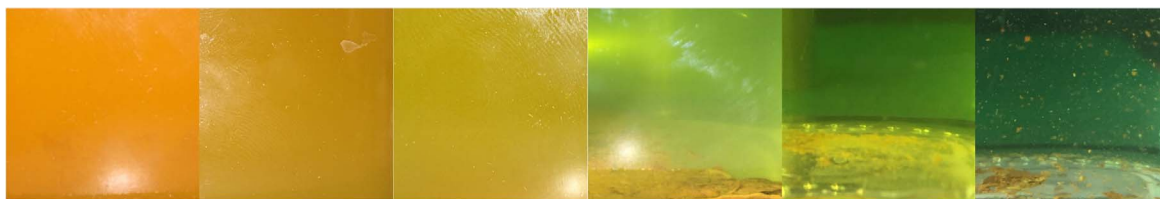


Figure 8. Color change of used electrolyte during a regeneration in a recombination cell with external hydrogen.

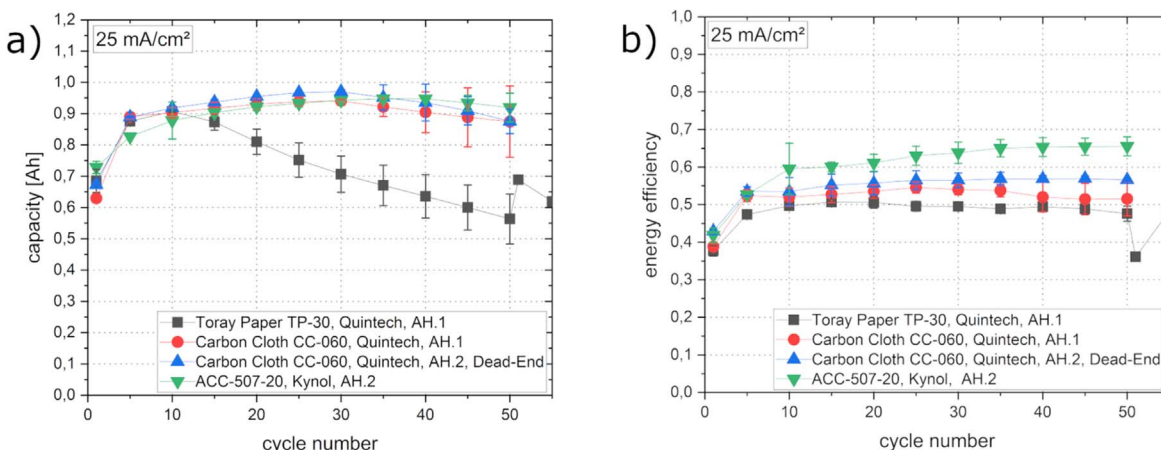


Figure 9. (a) Capacity and (b) energy efficiency of a Fe/Fe redox flow battery with different substrate materials for iron deposition (0.2 M HCl, 25 mA cm⁻², RC-Cell, $t_{\text{charge,max}} = 1$ h, $U_{\text{charge,max}} = 1.9$ V).

of the quantitative analyses, it can be assumed that the conversion was almost complete and that the loss can be kept constant over the number of regenerations using this method.

Further cell tests with recombination cells were carried out to investigate the battery properties of different substrate materials. Figure 9 shows the discharge capacities and the achieved energy efficiencies over 50 cycles.

In terms of discharge capacity, all materials, except Toray paper, behaved very similarly. The batteries with the Toray paper had a significantly higher capacity drop than the other materials because of visible solid Fe accumulation in the negative tank. The reason for the difference was probably an optimized test stand design and operation, where less hydrogen was lost. Typical for all other three materials is the initial increase of the discharge capacity to a value of about 0.95 Ah (95% capacity utilization) and a further slight drop in capacity due to probably hydrogen loss. Since the charging time was limited to 1 h and the maximum possible discharge capacity was 1.62 Ah, there was a surplus of capacity at the beginning, so that the capacities of the three materials were more linear at the beginning. With Toray paper, the loss was so high that this behaviour was not so clearly visible (see also Fig. 10a). In the energy efficiency curves shown in Fig. 9b, all of the materials had low energy efficiencies at the beginning due to the low pH value and the resulting hydrogen generation, due to low Coulomb efficiencies (not shown here) while the voltage efficiencies (not shown here) remained more or less constant. In the course of the 50 cycles, a dynamic equilibrium was achieved in which back diffusion of protons from the positive half-cell space into the negative half-cell space was approximately in equilibrium with the hydrogen produced at the negative electrode. With a maximum of 50%, Toray paper achieved the lowest maximum energy efficiency. A kynol fabric type ACC-507-20 achieved significantly higher values with a maximum of 65%. In between was another carbon fabric (CC-060, Quintech GmbH, Germany) with different spacers in the negative cell space (AH.1 & AH.2) and with a completely closed hydrogen exhaust (dead end) with approx. 55% energy efficiency.

In order to investigate the influence of the state of charge on the capacities, two further tests were carried out. Figure 10 shows the discharging capacities and the energy efficiencies of batteries with different end-of-charge criteria. In one experiment the charging time was limited to 1 h (SOC 60) and in another the time and voltage was set so high that the battery reached the final discharge voltage by polarisation due to concentration depletion (SOC 100). As can be seen in Fig. 10a, the batteries that were charged up to a maximum of 1 h had an initially increasing capacity curve. The batteries that were fully charged had a continuously decreasing capacity curve.

The difference is mostly a result of the two different charge methods. It can be explained by the fact that during the time limitation, initially a large part of the charge carriers is converted into hydrogen. With an increasing pH, Fe-deposition becomes more attractive and the capacity reaches a constant value over cycle number. Hydrogen or Fe losses will be hidden by the low capacity utilization but will probably follow the trend of the 100% charge after 50 cycles. When charged to a potential via constant current, the loss of charge carriers is manifested by an increased charging time and thus an increased charging capacity. The discharge capacity is higher and has a decreasing trend because of Hydrogen or Iron losses. The courses of the energy efficiencies of the two experiments shown in 10b were approximately the same within the scope of the measurement errors and amounted to up to 65%. The behaviour of the different discharge capacities is interesting in so far as for practical operation the charging strategies differ significantly and should be taken into account in the battery management system.

Figure 11 shows the behavior of Fe/Fe-RFBs at different current densities. As can be seen from the results in Fig. 11a, a battery at a current density of 12.5 mA cm⁻² (500 mA/40 cm²) had an average discharge power density of about 12.5 mW cm⁻². The energy efficiency was 70%. As the current density increased, the power density increased and the energy efficiency decreased due to cell resistance losses. At a current density of 75 mA cm⁻² (3 A/40 cm²) a battery achieved a power density of approx. 47 mW cm⁻² with an energy efficiency of 33%. The measurements were limited by the

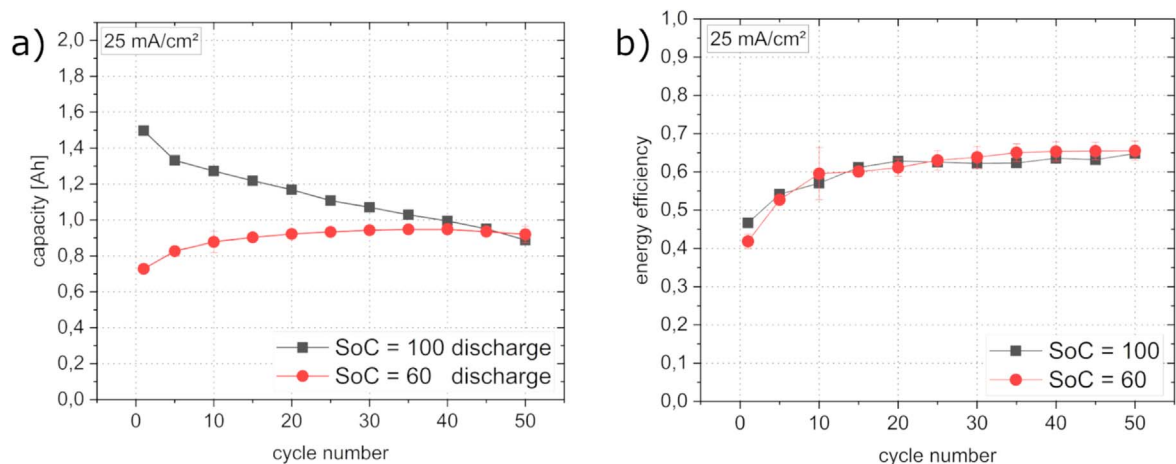


Figure 10. Discharge capacities of Fe/Fe redox flow batteries at different charge levels (25 mA cm⁻², 30/60 ml 1 M FeCl₂, 2 M NH₄Cl, 0.2 M HCl, Kynol ACC-507-20).

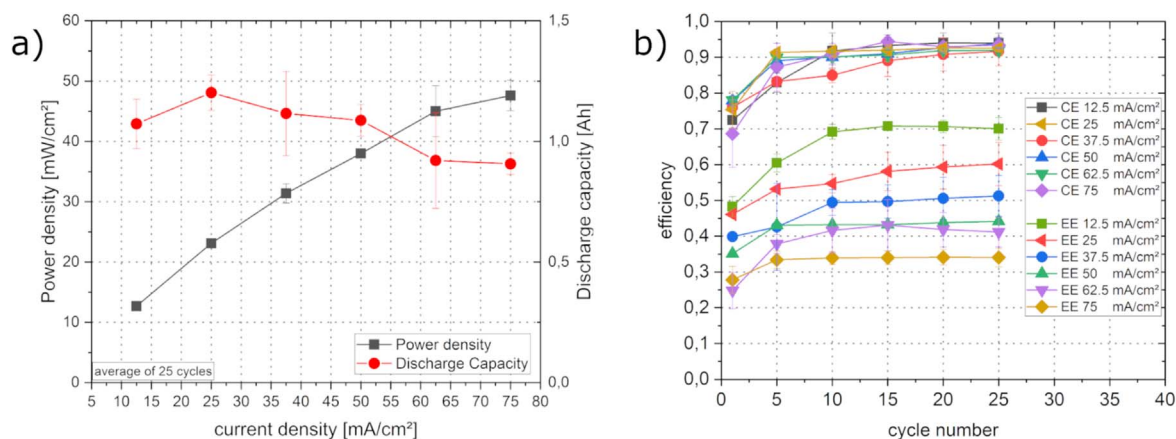


Figure 11 (a) Power densities and discharge capacities and (b) Energy and coulomb efficiencies of Fe/Fe redox flow-batteries at different current densities (30/60 ml 1 M FeCl₂, 2 M NH₄Cl, 0.2 M HCl, Kynol ACC-507-20).

performance of the potentiostat, so it can be assumed that the batteries could also convert higher currents at room temperature. However, the energy efficiencies were extremely low and future work will investigate the behaviour at higher temperatures to increase efficiencies and power densities. The discharge capacities were between 0.9–1.2 Ah. As expected, the capacities tended to decrease due to increasing IR-drop.

Figure 12 shows the coulomb and energy efficiencies of Fe/Fe redox flow batteries with different membranes. NAFION 115 is a cation exchange membrane, Fumatech FAP-450 is an anion exchange membrane, ASAHI SF-601 is a microporous separator and MPM is also a microporous separator with very low costs.

The coulomb efficiencies were relatively high for all batteries, with MPM achieving the lowest value at around 79%. ASAHI SF-601

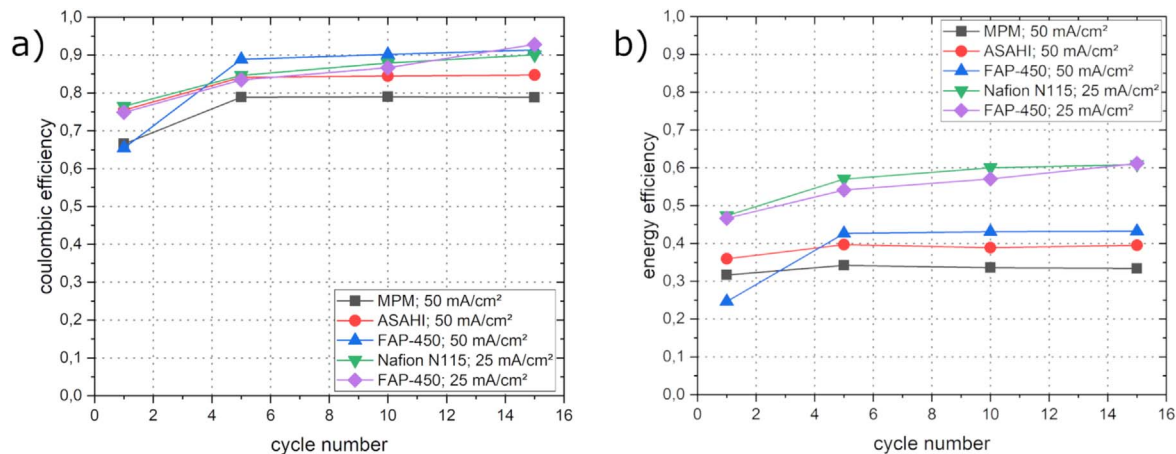


Figure 12. (a) Coulomb and (b) energy efficiencies of Fe/Fe redox flow batteries with different membranes.

achieved a slightly higher coulomb efficiency of 85% and the ion exchangers finally achieved even higher values of over 90%, as expected. The reason for this behaviour is the different selectivity of the different types of membranes. Microporous membranes have a low selectivity but often a low resistivity. Ion exchange membranes have a high selectivity and therefore a higher coulomb efficiency. Iron(III)-ions will migrate from the positive electrolyte to the negative and react with deposited Iron to Iron(II). This reaction is reversible and results in a loss in coulomb efficiency. A comparison of the coulomb efficiency of FAP-450 at different current densities also showed that the coulomb efficiency increases with the current density. On the one hand, this can mean that at higher overpotentials the iron deposition is more efficient or, on the other hand, that the diffusion of ions into the other half-cell space is reduced by shorter cycle times.

The conditions were similar for the energy efficiencies, with only low efficiencies of 33%–43% being achieved at 50 mA cm⁻². The microporous separator MPM achieved the lowest value, followed by ASAHI SF-601 and finally FAP-450 with the highest efficiency. At lower current densities the energy efficiencies increased to over 60%. Overall, the difference in the achieved efficiency values was smaller than expected. The biggest differences for the energy efficiencies were finally caused by the internal resistances and here especially by the negative reactions. Furthermore, it should be noted that there was no pressure control of the fluidic semi-circles. With such a control, higher coulomb efficiencies can probably be achieved with microporous separators. Finally, the results of techno-economic simulations must decide which of the membrane materials is more suitable.

Conclusions

Within the scope of this work and due to a small number of publications, the feasibility of an Fe/Fe redox flow battery was investigated. Due to the acidic electrolyte used here, there was a relatively high hydrogen evolution at the beginning of charging and discharging experiments. This resulted in a relatively high loss of capacity, which can be reduced by using a recombination cell. When using a recombination cell, a complex dynamic equilibrium is created by protons being transported into the positive half-cell, which must be further investigated to further reduce the capacity loss and increase the efficiency of the battery. Furthermore, in contrast to many other literature sources, cycle times of up to two hours were used here in order to be able to make statements as close to reality as possible. A battery with a recombination cell could be charged and discharged 100 times and lost about half its capacity. Regeneration experiments with external hydrogen showed that the loss was caused by hydrogen loss in the laboratory cell structure and that the capacity could be almost completely restored by regeneration. In further experiments, different substrate materials for iron deposition and different membranes were compared. Furthermore the effects of different current intensities were investigated. The substrate material had a significant influence on the efficiency values of the batteries. A Kynol fabric achieved the highest values with 65% energy efficiency. For the membranes, microporous separators, a cation exchange membrane (NAFION), and an anion exchange membrane (Fumatech FAP-450) were compared. Anion and cation exchangers achieved approximately the same energy efficiencies. As expected,

the microporous separators achieved lower values. In principle, the microporous separators are interesting because of their low costs. However, at 50 mA cm⁻² they achieved just 39% energy efficiency. Here, it was suspected that a large proportion of losses was caused by pressure differences in both half-cells and that this behaviour can be improved. At room temperature up to 47 mW cm⁻² of power density could be achieved with an energy efficiency of 33%. This was mainly due to the low kinetics of iron deposition and dissolution, together with the low Coulomb efficiency associated with recombination. Operation at elevated temperature and optimization of recombination could achieve significantly higher performance values, making this system very interesting for commercial use. However, a high development effort is still necessary in all aspects to achieve this goal.

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