Rational Cathode Design for High-Power Sodium-Metal Chloride Batteries

Gustav Graeber, Daniel Landmann, Enea Svaluto-Ferro, Fabrizio Vagliani, Diego Basso, Alberto Turconi, Meike V. F. Heinz,* and Corsin Battaglia

The transition from fossil fuels to renewable energy sources requires economic, high-performance electrochemical energy storage. High-temperature sodium-metal chloride batteries combine long cycle and calendar life, with high specific energy, no self-discharge, and minimum maintenance requirements, while employing abundant raw materials. However, large-scale deployment in mobility and stationary storage applications is currently hindered by high production cost of the complex, commercial tubular cells and limited rate capability. The present study introduces sodium-metal chloride cells with a simple, planar architecture that provide high specific power while maintaining the inherent high specific energy. Rational cathode design, considering critical transport processes and the effect of cathode composition on the cell resistance, enables the development of high-performance cells with average discharge power of 1022 W kg⁻¹ and discharge energy per cycle of 258 Wh kg⁻¹ on cathode composite level, shown over 140 cycles at an areal capacity of 50 mAh cm⁻². This corresponds to a 3.2C discharge over 80% of full charge. Compared to the best performing planar sodium-metal chloride cells with similar cycling stability and mass loading in the literature, the presented performance represents an increase in specific power by more than a factor of four, while also raising the specific energy by 74%.

1. Introduction

Transition from fossil fuels to renewable energy sources is imperative to reduce greenhouse gas emissions. Integrating renewable power generation based on solar and wind energy into the electricity grid requires scalable stationary energy storage solutions to match electricity production and demand. Similarly, for mobile applications, high-performance energy storage is required to provide alternatives for internal combustion engines burning fossil fuel.

High-temperature sodium-metal chloride batteries, also referred to as molten-salt batteries or Zebra batteries, are an excellent candidate for stationary energy storage since they provide long cycle and calendar life, require no maintenance, and employ abundant, non-critical raw materials without the need of Li, or Co.\(^{[1-3]}\) In principle, these qualities make them competitive with existing technologies such as lithium-ion or sodium-ion technology.\(^{[4,5]}\) However, large-scale deployment of sodium-metal chloride batteries is currently hindered by high production cost of the commercial tubular cells. Therefore, in the present work, we study sodium-metal chloride cells with a planar architecture. A transition from the commercial tubular design toward a planar cell design can reduce complexity in cell manufacturing and drastically lower assembly cost, making the sodium-metal chloride technology economically favorable to a wider range of applications, while it also poses mechanical design challenges.\(^{[6]}\) The feasibility of a planar cell design has been demonstrated for the past 15 years in numerous scientific publications.\(^{[7-19]}\) Beyond these important considerations on the cell design (tubular vs planar), it is the cathode composition and microstructure that is critical to the performance of a sodium-metal chloride cell. In contrast to lithium-ion batteries, which employ relatively thin electrodes (typically up to 100 µm),\(^{[20,21]}\) sodium-metal chloride batteries apply a cathode with considerable thickness (few millimeters), which gives rise to an increasingly important cell resistance contribution as the electrochemical reaction front progresses through the thickness of the cathode.\(^{[2]}\) As active cathode materials, previous studies on planar cell designs mostly focused on pure Ni cathodes and pure Fe cathodes,\(^{[7-10]}\) steadily increasing the specific energy, reaching up to 405 Wh kg⁻¹ on cathode composite level,\(^{[16]}\) and prolonging cycle life up to 1000 cycles.\(^{[18]}\) In further studies it was shown that the introduction of a mixed Fe/Ni cathode, where both Fe and Ni contribute to the cell capacity, can increase the power capability compared to cells with a pure Ni cathode.\(^{[2,22-23]}\) Multiple reasons support the use of mixed Fe/Ni cathodes, with the overall idea of combining the advantages of both metals. While Ni provides a
higher equilibrium potential, Fe is considerably cheaper than Ni, improving the economic competitiveness of sodium-metal chloride cells. Furthermore, it is known that the reaction kinetics of Fe are faster than Ni in sodium-metal chloride cells.[11] Finally, a mixed Fe/Ni cathode provides two possible electrochemical reactions that can be executed in parallel, thereby stabilizing the cell voltage in case of load peaks also at low state of charge (SOC).[2] Against this background it seems not surprising that for the past 20 years a mixed Fe/Ni cathode has been employed in commercial tubular cells.[2,24] However, our current understanding on how the cathode composition affects the cell performance remains incomplete.

Irrespective of the cathode composition, to date literature on sodium-metal chloride batteries was not able to demonstrate planar cells that simultaneously show high specific power, high specific energy, good energy efficiency, and high cycling stability. Such batteries are especially desirable for stationary energy storage in the context of grid balancing, where high power is required, or also in mobile applications including electric vehicles. Furthermore, critical insight into the electrochemically limiting cathode processes is missing, which is the key for further performance enhancement.

In the present study, we investigate how the cathode composition affects the accessible power, energy, and energy efficiency in planar sodium-metal chloride cells. We compare planar cells with Fe/Ni cathodes to cells with pure Ni cathodes, and study the effective cell resistance as a function of SOC, thereby providing a mechanistic insight into the relevant cell reactions. The cell resistance is of fundamental importance since—at a defined current—it determines the available capacity within given voltage limitations, and it directly affects the energy efficiency of the cell. With our analysis, we provide experimental evidence for a reaction front mechanism within the cathode, which was previously postulated in the literature and investigated using neutron diffraction imaging technique.[2,25–27] From our electrochemical data, we derive how the location of the cell reactions moves along the depth of the cathode, from the solid electrolyte to the current collector. Finally, we compare our cycling results to previously reported planar sodium-metal chloride cells. Thereby we show how a rational cathode design regarding composition and microstructure is guided by a mechanistic understanding of electrochemical activity of species and transport processes and provides a pathway towards substantial performance enhancements in sodium-metal chloride batteries.

2. Results and Discussion

For the present work, we developed planar sodium-metal chloride lab cells that we cycled at 300 °C, see Figure 1 and Section 4 for details. We compared two cathode compositions, namely mixed Fe/Ni cathodes and pure Ni cathodes.

We first discuss the performance of cells with a mixed Fe/Ni cathode. In Figure 2a, we show the galvanostatic maiden charge of the Fe/Ni cell at 3 mA cm$^{-2}$ (C-rate 0.05C). Analogous to previous studies, we define the theoretical capacity of the cell resistance is of fundamental importance since—at a defined current—it determines the available capacity within given voltage limitations, and it directly affects the energy efficiency of the cell. With our analysis, we provide experimental evidence for a reaction front mechanism within the cathode, which was previously postulated in the literature and investigated using neutron diffraction imaging technique.[2,25–27] From our electrochemical data, we derive how the location of the cell reactions moves along the depth of the cathode, from the solid electrolyte to the current collector. Finally, we compare our cycling results to previously reported planar sodium-metal chloride cells. Thereby we show how a rational cathode design regarding composition and microstructure is guided by a mechanistic understanding of electrochemical activity of species and transport processes and provides a pathway towards substantial performance enhancements in sodium-metal chloride batteries.

2. Results and Discussion

For the present work, we developed planar sodium-metal chloride lab cells that we cycled at 300 °C, see Figure 1 and Section 4 for details. We compared two cathode compositions, namely mixed Fe/Ni cathodes and pure Ni cathodes.

We first discuss the performance of cells with a mixed Fe/Ni cathode. In Figure 2a, we show the galvanostatic maiden charge of the Fe/Ni cell at 3 mA cm$^{-2}$ (C-rate 0.05C). Analogous to previous studies, we define the theoretical capacity of the cell
Figure 2. Galvanostatic cycling of planar sodium-metal chloride cells with mixed Fe/Ni cathode. a) Voltage versus specific capacity during maiden charge, highlighting the three metal chlorination reactions (Al, Fe, and Ni). b) Voltage versus specific capacity during the first three cycles. c) Symmetric rate test: Voltage versus specific capacity; charge and discharge rates increase symmetrically from 6 to 20 mA cm\(^{-2}\), three cycles per rate. Transition during charge from low-voltage to high-voltage plateau is highlighted. d) Discharge rate test: Voltage versus specific capacity; charge rates are constant at 20 mA cm\(^{-2}\), discharge rates increase from 20 to 80 mA cm\(^{-2}\), three cycles per rate. e) Cell resistance during charge computed from charge curves in (c). Within voltage transition region (15% to 30% SOC), accurate resistance computation is hindered by non-ohmic cell behavior, see Figure S2, Supporting Information. f) Cell resistance during discharge computed from discharge rate test in (d).
based on the electrochemical reactions of NaCl with the metal constituents in the cathode, namely Al, Fe, and Ni. For the Fe/Ni cell, the upper cut-off voltage was fixed to 2.75 V to avoid undesired overcharge reactions (Fe + 3 NaAlCl₄ ↔ FeCl₃ + 3 AlCl₃ + 3 Na at ≈ 2.75 V).

During maiden charge of the Fe/Ni cell, we distinguish three main reactions. Reaction 1: Oxidation of Al and formation of NaAlCl₄ and Na, given as:[28]

\[
\text{Al} + 4\text{NaCl} \leftrightarrow \text{NaAlCl}_4 + 3\text{Na} \quad \text{at } \approx 1.6 \text{ V (300 °C)}
\]

This reaction is applied irreversibly in our system, taking place exclusively during maiden charge. Formation of molten NaAlCl₄ from NaCl at the cathode improves the distribution of NaAlCl₄ within the granules, leading to enhanced electrochemical activity of the cathode. We thus fix the lower cut-off voltage at 1.6 V. Since we are performing a capacity-limited cycling protocol (see details below), the upper and lower cut-off voltages are typically not reached. Based on the amount of Al in the cathode composition (see Section 4), reaction 1 is limited to a maximum 15 mAh g⁻¹, until the entire Al content is consumed.

Subsequently, in the Fe/Ni cells, reaction 2: Oxidation and chlorination of Fe is initiated:[28]

\[
\text{Fe} + 2\text{NaCl} \leftrightarrow \text{FeCl}_2 + 2\text{Na} \quad \text{at } 2.32 \text{ V (300 °C)}
\]

Based on the amount of Fe in the Fe/Ni cathode, reaction 2 can provide a maximum of 63 mAh g⁻¹. At even higher cell voltage, we observe reaction 3: Oxidation and chlorination of Ni, given as:[2]

\[
\text{Ni} + 2\text{NaCl} \leftrightarrow \text{NiCl}_2 + 2\text{Na} \quad \text{at } 2.57 \text{ V (300 °C)}
\]

The equilibrium potentials for reaction 2 and 3 were derived from dedicated experiments by determining the open-circuit voltage (OCV) versus SOC using a galvanostatic intermittent titration technique (GITT), refer to Figure S1, Supporting Information for details.

In contrast to reaction 1 and 2, chlorination of Ni is not limited by the amount of Ni in the cathode. Instead, it is limited by the availability of NaCl in the cathode granules. Considering the amounts of NaCl consumed during reaction 1 and reaction 2 in the Fe/Ni cells, a capacity of 95 mAh g⁻¹ is expected from Ni chlorination, before the entire NaCl content in the cathode granules is consumed. We consider the 15 mAh g⁻¹ from reaction 1 as irreversible in our experiments, and assign it with negative values within the SOC window – see Figure 2a. In the Fe/Ni cells, the cumulative contributions from chlorination of Fe and Ni amount to a reversible theoretical capacity of 159 mAh g⁻¹ (100% SOC), with 40% SOC available at 2.32 V (reaction 2), and 60% available at 2.57 V (reaction 3). As is common in state-of-the-art literature on sodium metal chloride cells,[8,16] we consider the amount of granulated material added to the cathode (Ni, Fe, Al, NaCl, and additives) when computing the gravimetric capacity, while the liquid secondary electrolyte NaAlCl₄, the Ni foam and Ni pistons are not included in the calculation – see Note S1, Supporting Information: Ni foam. Corresponding values on cell level depend on the specific cell design.[50] For the Fe/Ni cells, the theoretical capacity of 159 mAh g⁻¹ translates into an areal capacity of 51 mAh cm⁻² (based on the solid electrolyte surface) at a mass loading of 0.32 g cm⁻².

Inspection of Figure 2a shows that the full theoretical capacity (corresponding to 100% SOC) can be obtained during the capacity-limited, galvanostatic maiden charge at voltages well below the upper cut-off voltage. For the Fe/Ni cells, we observe two pronounced voltage plateaus, featuring low overpotentials (+10 mV) compared to the equilibrium potentials, with the low-voltage plateau associated with Fe chlorination at low SOC, and the high-voltage plateau associated with Ni chlorination at high SOC. However, the high voltage edge (defined as the onset and ending of the high-voltage plateau during charge and discharge, respectively) occurs at a lower SOC (25% SOC) than theoretically possible (40% SOC), considering the iron content of the cathode. Chlorination of the remaining iron requires higher overpotentials, and takes place together with Ni chlorination in the high-voltage plateau.

In the subsequent cycles shown together with the maiden cycle in Figure 2b, we restrict the SOC window to a lower limit of 10% SOC, and to an upper limit of 90% SOC, providing a cycled capacity of 127 mAh g⁻¹. Despite the low current density applied (3 mA cm⁻², 0.05C), we observe a pronounced hysteresis in the voltage profile of the Fe/Ni cells between charge and discharge, manifesting itself in a shift of the high-voltage edge to higher SOC during discharge. The hysteresis results in substantially lower cell voltages during discharge than during charge at intermediate SOC (between 25% and 50% SOC), thereby reducing the roundtrip energy efficiency (further discussion below). During the second and third discharge, the high-voltage edge gradually moves to lower SOC (from 55% to 40% SOC). We ascribe this evolution of the discharge voltage profile to run-in processes within the cathode. Run-in processes can include a stabilization of the Fe/Ni cathode microstructure, where cycling enables a redistribution and improved contacting of the Fe and Ni particles forming the electronic backbone.[29,30] These effects are superimposed with the cell response to the SOC window reduction from the full SOC window in the first cycle down to 10% to 90% SOC in the following cycles. Changing the SOC window results in other locations of the cathode to participate in the electrochemical reactions[2] (see also discussion on reaction front mechanism below). Furthermore, we observe that the transition from the low-voltage Fe to the high-voltage Ni plateau takes place via different steps, indicating several intermediate processes. Based on literature, these steps can be related to a contribution of additives (e.g., FeS + 2 NaCl + Ni ↔ FeCl₃ + NiS + 2 Na at 2.37 V and Ni + 2 NaF ↔ NiF₄ + 2 Na at 2.39 V)[22] and to the formation of intermediate phases (e.g., Na₃FeCl₆).[10,26] Interestingly, we can distinguish two intermediate plateaus during charge, while during discharge there are three separate kinks in the transition region between low- and high-voltage plateau. During charge, these intermediate plateaus are shorter and the voltage trace makes a steeper transition between the low- and high-voltage plateau, indicating substantial overpotentials. As a result, the intermediate reactions mainly take place in the high-voltage plateau during charge, together with the chlorination of Ni. During discharge, the individual plateaus are differentiated according to their reaction potentials. In the future, further investigation is required to fully resolve the details of these transition reactions.
Figure 2c shows the voltage profiles of the Fe/Ni cell during a subsequent rate test, where we increase the charge and discharge rates symmetrically in four steps from 6 mA cm\(^{-2}\) (0.1C) to 20 mA cm\(^{-2}\) (0.4C). For each current density, we perform three cycles. The corresponding voltage profiles overlay almost ideally at each current density, indicating no further microstructural changes in the cathode. However, the increasing C-rates affect the characteristics of the hysteresis observed in the voltage profiles during charge and discharge. In particular, both in charge and discharge, the high-voltage edge shifts to lower SOC with increasing C-rates (by about 5 mAh g\(^{-1}\) between 0.1C and 0.4C). During charge, the shift of the high-voltage edge can be understood based on the increasing overpotentials associated with increasing charge currents. The higher the charge current, the higher the overpotentials, and the earlier (at lower SOC) the Ni chlorination is enabled. Our cycling data in Figure 2c shows that, in the subsequent discharge, more NiCl\(_2\) is available for dechlorination, which enables the observed shift of the high-voltage edge to lower SOC. This leads to the intriguing insight, that in Fe/Ni cells the ratio of Ni and Fe species undergoing oxidation/reduction depends on the current density applied during charge, and higher amounts of Ni are chlorinated at higher charge rates.

In Figure 2d, we maintain a constant charge rate of 20 mA cm\(^{-2}\) (0.4C) to respect the upper cut-off voltage, but further increase the discharge rate in four steps from 20 mA cm\(^{-2}\) (0.4C), up to 80 mA cm\(^{-2}\) (1.6C). Again, three cycles per rate are performed, resulting in overlying voltage profiles, indicating a stable cathode microstructure. In contrast to Figure 2c, the high-voltage edge is no longer subject to a shift during discharge at the different rates, since the constant charge rates lead to the same degree of Ni chlorination, confirming the conclusion above. For the highest discharge rates of 1.6C, the cell voltage falls to values of around 2.1 V. Remarkably, we find that the voltage traces during charge shown in Figure 2c and the voltage traces during discharge shown in Figure 2d follow an almost ideal linear (ohmic) relation with the applied currents (see Figure S2, Supporting Information). Only in the transition region between low-voltage and high-voltage plateau (highlighted in Figure 2c) deviations from linearity between the voltage traces reach values above 1% (see Figure S2, Supporting Information). Thus, non-linear polarization resistances are negligible, and we can derive the relevant effective cell resistances for charge and discharge in our cells based on a simple linear interpolation, as described in more detail in Note S2, Supporting Information: Resistance Computation. We present the computed cell resistance during charge and discharge as a function of SOC in Figure 2e,f, respectively. In both cases, we identify a base resistance of around 0.6 \(\Omega\) (1.9 \(\Omega\) cm\(^2\)), which is present independently of SOC. The base resistance comprises the resistances related to passive cell components, Na-β″-alumina solid electrolyte, and even anode processes, which did not show an SOC-dependency in a previous study.\(^{[31]}\) Thus, we can ascribe the SOC-dependent, variable resistance contributions as observed both for charge and discharge in Figure 2e,f to cathode processes.

In Figure 3, we show schematics of the cathode chlorination and dechlorination processes during charge and discharge explaining these SOC-dependent resistance contributions from the Fe/Ni cathode. The cathode is composed of a porous percolating network of the Ni and Fe particles. The channels in the
network are filled with the liquid NaAlCl₄ secondary electrolyte ensuring the transport of Na ions. For Fe/Ni cells, during charge at low SOC (Figure 3a), Fe chlorination starts from the Na-β-alumina solid electrolyte interface, and progresses across the cathode towards the current collector. The initiation of the reaction front directly at the Na-β-alumina solid electrolyte interface and its movement into the depth of the cathode were experimentally shown with high spatial resolution using neutron diffraction technique.[28] The more the Fe chlorination reaction front advances, the longer the transport path for the Na ions through the liquid NaAlCl₄ secondary electrolyte from the reaction site to the Na-β-alumina solid electrolyte, which results in increasing cell resistance (Figure 2e, 10–15% SOC). Exclusively the Na ions have to travel from the reaction site to the Na-β-alumina solid electrolyte interface, while the Fe ions, the Ni ions and the Cl ions required for the reactions are evenly distributed over the entire depth of the cathode. Towards the end of Fe chlorination, the overpotentials rise substantially, which we ascribe to limited accessibility of the remaining Fe in the cathode microstructure, resulting in a rapid rise in cell resistance, as seen in Figure 2e at 20–25% SOC. The high cell resistance for Fe chlorination in this transition region, together with a contribution of additives, is seen as a main cause for the hysteresis observed in the charge/discharge behavior in Fe/Ni cells. At a later stage, the transport resistances required to continue Fe chlorination result in an increase of the cell potential to above the equilibrium potential of Ni chlorination, which is then initiated, thereby reducing the cell resistance, as seen in Figure 2e at 30% SOC. During charge at high SOC (Figure 3b), Ni chlorination starts from the Na-β-alumina solid electrolyte interface, and progresses across the cathode towards the current collector. The more the Ni chlorination reaction front advances into the cathode, the longer the transport paths for the Na ions through the liquid NaAlCl₄ secondary electrolyte, which results in a continuous increase in cell resistance, as seen in Figure 2e from 30% to 90% SOC. However, the resistance increases non-linearly. This can be associated with the volumetric expansion of the Fe and Ni due to the metal chlorination. In fact, chlorinating Fe and Ni to FeCl₂ and NiCl₂ results in a volume increase by more than a factor of two and the formation of lamellar structures in the cathode that occupy a considerable amount of space as was shown via SEM on charged cells.[32] This can result in obstructions that further increase the required transport path for the Na ions (Figure 3b). A tailored cathode porosity that can accommodate this volumetric expansion and prevent obstructions to cause even further increases in cell resistance is critically important. To illustrate this fact, we performed dedicated experiments, where we compare granulated cathode material to a non-granulated cathode pellet (see Note S3, Supporting Information: Granulation, and Figure S3, Supporting Information). These experiments showed that only a granulated cathode can ensure effective ionic transport, thereby reducing overpotentials to an acceptable level.

During discharge, dechlorination starts with NiCl₂, but again proceeds from the Na-β-alumina solid electrolyte interface, across the cathode, towards the current collector (Figure 3c). While during charge, obstructions in the cathode related to the chlorination were hindering Na ion transport leading to a rise of the cell resistance beyond a linear increase, no such effect is observed during discharge. In fact, the dechlorination progresses away from the solid electrolyte and thereby simultaneously removes the obstructions. Therefore, as the NiCl₂ dechlorination front proceeds, the cell resistance rises linearly (Figure 2f) until the cell voltage drops below the equilibrium potential of FeCl₂ dechlorination, which is then initiated (Figure 3d). The initiation of FeCl₂ dechlorination reduces the effective cell resistance in Figure 2f at 20% SOC. Within the transition region between the NiCl₂ dechlorination and FeCl₂ dechlorination, there is a small intermediate peak in the resistance profile at around 25% SOC, which we attribute to the fluorine added as an additive in the cathode granules as discussed above, where Ni + 2 NaF ↔ NiF₂ + 2 Na at a cell voltage of 2.39 V.[24] In summary, this reaction front mechanism (Figure 3) explains the non-monotonic resistance behavior in Figure 2e,f. These mechanistic insights enable us to understand why a mixed cathode with Fe and Ni can reduce the cell resistance in specific SOC domains, and how cathodes can be tailored to different demands in specific power and energy. Our analysis also demonstrates a strong increase in cathode resistance in the transition region, which originates from the two spatially separated reaction fronts (associated with Fe and Ni oxidation and reduction) propagating across the depth of the cathode compartment. This results in a hysteresis in the voltage traces of charge and discharge, reducing the energy efficiency in this SOC range. This has to be taken into account when deciding for or against the use of Fe in the cathode. Given the mixed consequences of using Fe in the cathode, it is natural to compare the obtained results to pure Ni cathodes.

We present the results for the Ni cells in Figure 4. In the absence of Fe, only reaction 1 and reaction 3 occur, and no Fe overcharge reaction can take place. This allows setting the upper cut-off voltage to 3.05 V, above which decomposition of NaAlCl₄ would result.[3] Based on the cathode composition of the Ni cells (see Experimental section), we expect an irreversible capacity contribution based on reaction 1 of ≈15 mAh g⁻¹, until the entire Al content is consumed. The remaining NaCl in the cathode could ideally provide a total reversible capacity of 169 mAh g⁻¹ based on reaction 3. This theoretical capacity of 169 mAh g⁻¹ for the studied Ni cells slightly exceeds the theoretical capacity of the Fe/Ni cells and translates into an areal capacity of 54 mAh cm⁻² at a mass loading of 0.32 g cm⁻². For an easier comparison between the two cathode compositions, we define state of charge (SOC) based on the theoretical capacity of the Fe/Ni cells.

In Figure 4a, we show the maiden charge of a Ni cell. In contrast to the Fe/Ni cells, we observe only a single voltage plateau associated with reaction 3. In Figure 4b, we show the first three cycles of the Ni cell, compared to the data from the Fe/Ni cells. Also for the Ni cells, we limit the cycling window between 10% and 90% SOC. The Ni cell immediately shows a stable voltage change in discharge potentials in the Fe/Ni cells during the first three cycles stems from a redistribution of Fe in the cathode microstructure. A contribution of additives is not observed in the Ni cell, since the cell voltage remains above 2.39 V. Towards the end of discharge, the cell voltage begins to decrease, indicating increasing internal cell resistances. Interestingly, both charge and discharge voltage in the Ni plateau are higher for
Figure 4. Galvanostatic cycling of planar sodium-metal chloride cells with Ni cathode. a) Voltage versus capacity during maiden charge, highlighting the two metal chlorination reactions (Al and Ni). b) Voltage versus capacity during the first three cycles. c) Symmetric rate test: Voltage versus specific capacity; charge and discharge rates increase symmetrically from 6 to 20 mA cm$^{-2}$, three cycles per rate. d) Discharge rate test: Voltage versus specific capacity; charge rates are constant at 20 mA cm$^{-2}$, while discharge rates increase from 20 to 160 mA cm$^{-2}$, three cycles per rate. e) Cell resistance during charge computed from voltage traces in (c). f) Cell resistance during discharge computed from voltage traces in (d) (considering 20–80 mA cm$^{-2}$). In (a), (b), (e), and (f), the corresponding data from the Fe/Ni cell is shown for reference.
the Ni cell than for the Fe/Ni cell. Based on dedicated GITT measurements, we find a slightly higher OCV in the high-voltage plateau for the pure Ni-cell of 2.58 V, compared to the 2.57 V measured for the Fe/Ni cell (see Figure S1, Supporting Information). The presence of Fe has previously been reported to decrease the cell potential in the Ni plateau, where it was ascribed to the presence of Ni$_2$Fe$	ext{Cl}_6$.[33] Alternatively, it is also possible to consider a mixed electrode potential versus Na$^+$/Na (see reaction 2).[33]

In Figure 4c,d, we show a rate test for the Ni cathode, which is mostly analogous to the Fe/Ni cells (Figure 2). For the Ni cells, we observe no plateau shifts, since only reaction 3 is performed. Furthermore, as shown in Figure 4d, the pure Ni cathodes enable even higher discharge rates than the Ni/Fe cells, allowing us to include four additional discharge rate steps ranging from 100 mA cm$^{-2}$ (2C) up to 160 mA cm$^{-2}$ (3.2C). Since only the high-voltage reaction 3 is performed, the potential stays comparably high also at low SOC, and for double the discharge rate we can still limit the potential drop to similar amounts as for the Fe/Ni cells (Figure 2). Just like the Fe/Ni cells, also the Ni cells exhibit a linear (ohmic) relation with the applied currents during charge and discharge. For the Ni cells, the deviation from linearity remains below 0.2% during charge and only exceeds 0.5% at the very end of discharge (see Figure S4, Supporting Information). Therefore, also for the Ni cells, we can easily compute the cell resistances versus SOC for charge and discharge (Figure 4e,f). To facilitate comparison to the Fe/Ni cells, we compute the resistance based on the discharge traces between 20 and 80 mA cm$^{-2}$. In contrast to the Fe/Ni cells, the Ni cells show a monotonic increase in resistance as SOC increases during charge and as SOC decreases during discharge, since only a single electrochemical reaction is performed. Only in the very beginning of the charge and discharge, we see a minor dip in the resistance of the Ni cells that might be related to start-up processes due to the abrupt increase in current. This effect is especially relevant at high currents (Figure 4c,d). Both at the end of charge and discharge, we find a steep increase in resistance related to limited accessibility of reaction sites, illustrating the benefit of the established capacity limitations. Cycling beyond these limits would be inefficient due to considerably increasing resistances.

We summarize the rate capability of both types of planar sodium-metal chloride cells in Figure 5. For each cycle of the rate test, we show the specific energy for charge and discharge, and the calculated roundtrip energy efficiency, as obtained by galvanostatic, capacity-limited cycling between 10% SOC and 90% SOC (Figure 5a,b). For the Fe/Ni cells, due to increased overpotentials at higher current densities, the discharge energy decreases from 315 to 292 Wh kg$^{-1}$ when increasing the discharge rates from 0.1C to 1.6C, with energy efficiencies of 97% and 89%, respectively. For the Ni cells, the discharge energies range between 325 and 281 Wh kg$^{-1}$ when increasing the discharge rates from 0.1C to 3.2C, with energy efficiencies between 99% and 84%, respectively. Figure 5c,d show the corresponding specific power during charge and discharge, averaged over the entire capacity window between 10% SOC and 90% SOC, as a function of the cycle number. We first discuss the Fe/Ni cells: While for a discharge current of 6 mA cm$^{-2}$ (0.1C) the average discharge power results in 47 W kg$^{-1}$, during the fast discharge at 80 mA cm$^{-2}$ (1.6C), we obtain an average discharge power of 580 W kg$^{-1}$. Within the high-voltage plateau, the maximum discharge power even reaches 608 W kg$^{-1}$, while at the end of the low-voltage plateau the discharge power is around 530 W kg$^{-1}$ (see Figure S5, Supporting Information). When discharging the Ni cells at 80 mA cm$^{-2}$ (1.6C), we obtain a slightly higher average discharge power of 598 W kg$^{-1}$, due to the higher average cell potential of the Ni cell. The measured power of the Ni cells further increases to 1105 W kg$^{-1}$ when discharging at 160 mA cm$^{-2}$ (3.2C). Since during discharge of the pure Ni cells only the high-voltage Ni dechlorination is performed (and no low-voltage Fe dechlorination), the cell potential stays high over the entire SOC window. This enables even higher discharge rates by avoiding conflicts with the lower cut-off voltage.

In Figure 6a–f, we show high-power discharging of our sodium-metal chloride cells, while applying a charge rate of 15 mA cm$^{-2}$ (0.3C). Over a total of 50 cycles, the Fe/Ni cell supplies an average specific discharge energy of 277 Wh kg$^{-1}$ at an average discharge power 550 W kg$^{-1}$, when discharged at 80 mA cm$^{-2}$ (1.6C). The fading observed in Figure 6b over the 50 cycles illustrates that these conditions stress the Fe/Ni cell and lead to degradation. In contrast, the Ni cell supplies an average specific discharge energy of 258 Wh kg$^{-1}$ at an average discharge power 1022 W kg$^{-1}$, when discharged at 160 mA cm$^{-2}$ (3.2C), with only minor signs of degradation over a total of 140 cycles.

In Figure 6g, we compare the performance achieved in the present study to reports on planar Na-NiCl$_2$ and Fe-NiCl$_2$ cells by showing specific discharge energy versus specific discharge power with respect to the cathode granule weight in a Ragone plot. We show data from the rate test in Figure 5, as well as the average of the 50 cycles for the Fe/Ni cathode (error bars represent the maximum and the minimum value obtained over the 50 cycles), and the average of the 140 cycles for the Ni cathode. In literature, we find data from both high-temperature experiments (around 300 °C), and from intermediate temperature experiments (around 190 °C). We can further distinguish two main groups, based on the number of cycles demonstrated. We define a first group with long-term studies, showing more than ten cycles (typically between 50 and 300 cycles, represented in Figure 6g by solid symbols). The majority of these studies achieved a specific discharge power below 100 W kg$^{-1}$. To date, the highest specific power in the long-term cycling group is 220 W kg$^{-1}$, achieved over 60 cycles at a temperature of 280 °C and at a specific energy of 148 Wh kg$^{-1}$.[9] Comparing this to our present Fe/Ni cell result, we find that we were able to increase the specific power by more than a factor two, while simultaneously increasing the specific energy by 87%. More importantly, our Ni cell could increase the specific power by more than a factor four compared to Ref. [9], while increasing the specific energy by 74%. In the second group, we present studies showing short-term cycling of equal or less than ten cycles (represented in Figure 6g by open symbols). Here, the specific power ranges between 100 and 750 W kg$^{-1}$.[13] Interestingly, there is a roughly linear trend in the Ragone plot for the short-term cycling group from literature, where the specific energy drastically decreases with increasing specific power. By plotting our rate test results with three cycles per data point from Figure 5 into the Ragone plot, we can show that in our
cells with the capacity-limited cycling protocol, the specific energy is more stable against increasing the power. Comparing our results both against long-term and short-term cycling results from the literature illustrates the strengths of the proposed cells.

While for cells with a mixed Fe/Ni cathode, charge rates are limited to comparably low current densities due to the risk of starting a Fe overcharge reaction at approximately 2.75 V, cells without Fe in the cathode can be charged substantially faster. We demonstrate this in Figure 7. In Figure 7a, we show a rate test with charge rates increasing from 20 up to 110 mA cm$^{-2}$, which corresponds to a C-rate above 2C. As shown in Figure 7b, we can achieve these high charge rates combined with discharge rates of 160 mA cm$^{-2}$ at energy efficiencies of around 80%. For this high-power cycling, both charge and discharge power range around 1000 W kg$^{-1}$ (Figure 7c). By comparing this performance to the existing results on planar Na-NiCl$_2$ and Fe-NiCl$_2$ cells, we find that this represents a remarkable increase. To date, the highest reported charge rates for planar sodium-metal chloride cells are 30 mA cm$^{-2}$ (corresponding to a specific charge power of 239 W kg$^{-1}$) at a specific capacity of 90 mAh g$^{-1}$.[9] We can conclude that the Ni cells in the present study with a charge rate of 110 mA cm$^{-2}$ (corresponding to a specific charge power of 976 W kg$^{-1}$) at a specific capacity of 127 mAh g$^{-1}$ provide a substantial increase in specific charge power by more than a factor four while simultaneously increasing the specific capacity by more than 40%.

3. Conclusion

We compared planar sodium-metal chloride cells with Fe/Ni cathodes to cells with pure Ni cathodes. Based on rate tests, we found an ohmic cell behavior over the majority of the cycling window irrespective of composition. By analyzing the effective cell resistance, we showed that combining Fe and Ni in the cathode allows to initiate two individual reaction fronts progressing across the cathode. As a result, the effective cell resistance shows a non-monotonic behavior versus state of charge (SOC). Such cells with Fe/Ni cathodes showed
Figure 6. High-power discharging. a–c), Fe/Ni cathode: a) Cell voltage versus specific capacity (charging at 15 mA cm$^{-2}$, 0.3C, and discharging at 80 mA cm$^{-2}$, 1.6C, over 50 cycles, showing every 10th cycle). b) Specific energy charged and discharged, as well as energy efficiency. c) Averaged specific charge and discharge power. d–f), Ni cathode: d) cell voltage versus specific capacity (charging at 15 mA cm$^{-2}$, 0.3C, and discharging at 160 mA cm$^{-2}$, 3.2C, over 140 cycles, showing every 20th cycle). e) Specific energy charged and discharged, as well as energy efficiency. f) Averaged specific charge and discharge power. g) Ragone plot showing specific discharge energy versus specific discharge power of the present study as compared to literature. Performance shown for equal or <10 cycles is represented by open symbols, while more than ten cycles are represented with solid symbols. The theoretical areal capacity is ≈50 mAh cm$^{-2}$ in all studies except for Refs. [8,13] that study higher areal capacities (Table S1, Supporting Information).
Figure 7. High-power charge rate test of the Ni cathode. a) Voltage versus specific capacity, where discharge rates are constant at 160 mA cm\(^{-2}\), while charge rates increase from 20 mA cm\(^{-2}\) in steps of 10 up to 110 mA cm\(^{-2}\), with three cycles per rate. b) Corresponding specific energy charged and discharged, as well as energy efficiency versus cycle number, also highlighting the C-rates. c) Corresponding averaged, specific charge, and discharge power versus cycle number.

high specific discharge energy and power of 277 Wh kg\(^{-1}\) and 550 W kg\(^{-1}\), respectively, over a total of 50 cycles. Within the group of long-term cycling results in literature with more than ten cycles shown, the presented cell performance substantially exceeds previous reports on planar sodium-metal chloride cells, increasing specific power by more than a factor two, while simultaneously increasing the specific energy by 87\% as compared to the best performing cells to date. Remarkably, cells with pure Ni cathodes showed even higher specific discharge power of 1022 W kg\(^{-1}\), while maintaining a high specific discharge energy of 258 Wh kg\(^{-1}\) over a total of 140 cycles, thereby increasing the specific power by more than a factor of four over the state-of-the-art, while simultaneously increasing the specific energy by 74\%. Furthermore, Ni cathodes demonstrated also substantially enhanced charging performance with a specific power of 976 W kg\(^{-1}\) and a specific capacity of 127 mAh g\(^{-1}\). With our study we show that rationally designing the cathode based on mechanistic understanding of the involved electrochemical and transport processes provides a pathway to markedly increase the performance of the sodium-metal chloride technology. For future work it is necessary to study more dynamic cycling protocols and higher mass loadings to further probe the effect of cathode composition. Furthermore, it is desirable to develop solutions to transfer from lab cells (as used in the present study) towards commercial cell designs that are economically viable. This could enable a large-scale deployment of this powerful technology.

4. Experimental Section

Figure 1a shows a schematic cross-sectional view of the high-temperature planar sodium-metal chloride lab cell. Considerations on how to adapt such a cell design to maximize energy density on cell level for commercialization were discussed in Ref. [6]. The cells were assembled from two \(\alpha\)-alumina collars (99.7\% Al\(_2\)O\(_3\), inner diameter 20 mm) and one Na-\(\beta\″\)-alumina solid electrolyte disc. Na-\(\beta\″\)-alumina discs were prepared by pressing spray-dried Li-stabilized Na-\(\beta\″\)-alumina powder into disc-shaped green bodies with a diameter of 45 mm and a thickness of \(\approx 4\) mm. The green bodies were placed onto buffer green discs and sintered inside a ceramic encapsulation in static air at 1600 °C (Nabertherm HT 40/17, heating rate 3 K min\(^{-1}\), dwell time 5 min).\(^{[34]}\) Subsequently, the sintered Na-\(\beta\″\)-alumina discs were ground down to a thickness of 1 mm (Elb surface grinding machine with diamond blade and sample water cooling), cleaned in isopropyl alcohol, and dried in an oven under air at 100 °C. Inside a tube furnace at 300 °C, a conductivity of 0.2 S cm\(^{-1}\) was measured for the Na-\(\beta\″\)-alumina using electrochemical impedance spectroscopy (Zahner IM6, frequency 1 Hz to 1 MHz, amplitude 20 mV) in four-point-probe configuration (Figure S6, Supporting Information).\(^{[35]}\) Subsequently, the solid electrolyte discs were glass sealed between the two \(\alpha\)-alumina collars using a high-temperature glass sealing at 1010 °C (Carbolite CWF 1200, heating rate 3 K min\(^{-1}\), dwell time 5 min) to obtain the ceramic subassembly of the cell (Figure 1b,c). A K-type thermocouple was inserted into a slit machined into one of the \(\alpha\)-alumina collars to accurately measure the cell temperature. To avoid dewetting of Na from the sodiophobic Na-\(\beta\″\)-alumina surface, the anode side of the Na-\(\beta\″\)-alumina was spray coated with a porous carbon coating (composed of 7 wt\% carbon black, 11 wt\% sodium hexametaphosphate, 55 wt\% isopropanol, 27 wt\% water, and 0.3 wt\% acetone) using an airbrush system (Aztek, pressurized air, \(\approx 2\) bar) and dried at 280 °C in air (Carbolite CWF 1200, heating rate 5 K min\(^{-1}\), dwell time 5 min) to remove all remaining solvents (porosity and thickness of coating after drying \(\approx 80\%\) and 50 \(\mu\)m (inset in Figure 1c), respectively). Further details on the carbon coating can be found in Ref. [31]. Cell assembly and charge/discharge cycling was performed in an Ar-filled glove box (typically \(c_{CH2O} < 0.1\) ppm, \(c_O2 < 0.1\) ppm). The cathode compartment was filled with 1 g of millimeter-sized cathode granules. The materials were characterized based on Brunauer–Emmett–Teller (BET) measurements.
in a BET surface area analyzer. Two different cathode compositions were investigated: Fe/Ni granules (used in Cell A and Cell B, where during cycling Fe and Ni are electrochemically active) consist of the three metallic components Ni (50 wt%, filamentary Ni255, BET surface area: 0.64 m² g⁻¹), Fe (7 wt%, BET surface area: 0.15 m² g⁻¹), and Al (0.5 wt%, BET surface area: 0.16 m² g⁻¹). Furthermore, they contain micro-fine NaCl (39 wt%) and the following additives: FeS (2 wt%), NaF (2 wt%), and NaI (0.5 wt%). The addition of a small amount of Al to the cathode was discussed as beneficial since it can provide additional porosity.[8,22] The sulfur provided in the form of FeS was shown to prevent Ni particle growth during cycling[6] and can facilitate the initial activation of Fe and Ni.[10] Ni granules (used in Cell C and Cell D, where during cycling only Ni is electrochemically active) consisted of the two metallic components Ni (54 wt%, filamentary Ni255), and Al (0.5 wt%). Furthermore, they contained NaCl (42 wt%) and the following additives: FeS (2 wt%), NaF (2 wt%), and NaI (0.5 wt%). The granules were manufactured by mixing and compacting the raw materials using a laboratory roller press (Komarek BO50A, roll force 30 kN), granulated using a laboratory granulator (Komarek GI050A) and sieved to remove particles larger than 1.6 mm. Images from both granule types obtained via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) are presented in Figures S7, S8, Supporting Information. X-ray powder diffraction (XRD) analysis of the cathode materials is shown in Figure S9, Supporting Information. After filling the cathode compartment with the granules, 0.5 g of secondary electrolyte NaAlCl₄ (anhydrous, powder, 99.99%) were vacuum infiltrated into the granules at a pressure of <10 mbar and a temperature of 200 °C (dwell time ≈20 min) (Figure 1d). A Ni foam (99.5% purity, 1.6 mm thickness, 95% porosity) and additional 0.2 g of NaAlCl₄ were added to the cathode side. The rigid Ni foam served as both a current collector and NaAlCl₄ reservoir, compensating volume changes of the cathode material during charge/discharge cycling (Figure 1e) – see Note S1, Supporting Information: Ni foam. Into the anode compartment, a disc of 0.3 g of Na (99.9% purity, thickness ≈1 mm) was added. In principle, no initial Na was required on the anode side, as Na is generated electrochemically during the charging of the cell, and the porous carbon coating functions as electrode. However, excess Na facilitated formation cycling and the study of the cathode compartment on lab scale. Molten sodium plating and stripping dynamics was investigated in detail in a previous study demonstrating ultra-high current densities beyond 1000 mA cm⁻² without dendrite formation.[30] The anode and cathode compartments were closed with spring-loaded Ni pistons. The entire assembly was compressed between stainless steel top and bottom plates using six stainless steel bolts and aluminia washers for electrical insulation (Figure 1f). Ni-wires fixed by screws connected the backside of the Ni pistons with the stainless steel top and bottom plates to bypass the electrical resistance of the springs. Graphite seals placed between the α-alumina collars and the top and bottom plates were used to seal the cell towards the outside. The resulting active cell area was 3.14 cm², resulting in a cathode granule mass loading of 0.32 g cm⁻². Cells were charge/discharge cycled at 300 °C (Biologic VSP3e). The cell temperature during cycling was monitored and controlled with a precision of better than ±10 °C using a resistive coil heater (SAF KM-HC-GS).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Tu Lan for performing XRD measurements, Benjamin Kunz for assistance in experimental setup construction, and Erwin Pieper for assistance in cell fabrication. The Swiss Federal Office of Energy (SFOE) under contract number SI/501674 funded this work.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

G.G., D.L., M.V.F.H., and C.B. conceptualized the work and analyzed data. G.G., D.L., and E.S.F. performed and validated experiments. G.G., D.L., F.V., D.B., A.T., and M.V.F.H. provided methodology. G.G., D.L., E.S.F., M.V.F.H., and C.B. wrote the manuscript. M.V.F.H. and C.B. acquired the funding, administered the project and supervised the work.

Data Availability Statement

Research data are available from the corresponding author upon request.

Keywords

alkali metal anode, anode-free battery, energy storage, planar zebra battery, sodium-metal halide battery, sodium-nickel chloride battery

Received: July 19, 2021
Published online: August 15, 2021
[19] G. Li, X. Lu, C. A. Coyle, J. Y. Kim, J. P. Lemmon, V. L. Sprenkle, Z. Yang, J. Power Sources 2012, 220, 193.
[20] M. Uitz, M. Sternad, S. Breuer, C. Täubert, T. Traußnig, V. Hennige, I. Hanzu, M. Wilkening, J. Electrochem. Soc. 2017, 164, A3503.
[21] Y. Kuang, C. Chen, D. Kirsch, L. Hu, Adv. Energy Mater. 2019, 9, 1901457.
[22] R. C. Galloway, S. Haslam, J. Power Sources 1999, 80, 164.
[23] C.-W. Ahn, M. Kim, B.-D. Hahn, I. Hong, W. Kim, G. Moon, H. Lee, K. Jung, Y.-C. Park, J.-H. Choi, J. Power Sources 2016, 329, 50.
[24] R. Benato, N. Cosciani, G. Crugnola, S. Dambone Sessa, G. Lodi, C. Parmeggiani, M. Todeschini, J. Power Sources 2015, 293, 127.
[25] J. Rijssenbeek, H. Wiegman, D. Hall, C. Chuah, G. Balasubramanian, C. Brady, in 2011 IEEE 33rd Int. Telecommunications Energy Conf., IEEE, Amsterdam 2011.
[26] V. Zinth, S. Seidlmayer, N. Zanon, G. Crugnola, M. Schulz, R. Gilles, M. Hofmann, J. Electrochem. Soc. 2015, 162, A384.
[27] C. Daniel, J. O. Besenhard, Handbook of Battery Materials, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany 2011.
[28] R. J. Bones, J. Coetzer, R. C. Galloway, D. A. Teagle, J. Electrochem. Soc. 1987, 134, 2379.
[29] T. Javadi-Doodran, Microstructure and Conductivity of the Sodium Nickel Chloride (ZEBRA) Battery Cathode, McMaster University, Hamilton, Canada 2012.
[30] R. Christin, Multiphysics Modeling of Sodium Nickel Chloride Cells, Université Grenoble Alpes, Grenoble, France 2015.
[31] D. Landmann, G. Graeber, M. V. F. Heinz, S. Haussener, C. Battaglia, Mater. Today Energy 2020, 18, 100515.
[32] T. Javadi, A. Petric, J. Electrochem. Soc. 2011, 158, A700.
[33] G. P. Power, I. M. Ritchie, J. Chem. Educ. 1983, 60, 1022.
[34] M.-C. Bay, M. V. F. Heinz, R. Figi, C. Schreiner, D. Basso, N. Zanon, U. F. Vogt, C. Battaglia, ACS Appl. Energy Mater. 2019, 2, 687.