Cathode Materials of Sodium-Metal Chloride Batteries

The widespread electrification of various sectors is triggering a strong demand for new energy storage systems with low environmental impact and using abundant raw materials. Batteries employing elemental sodium could offer significant advantages, as the use of a naturally abundant element such as sodium is strategic to satisfy the increasing demand.

1. Standard Active Cathode Materials

Various metal halides have been investigated as redox couples for ZEBRA batteries; however, among them, sodium-nickel chloride-based cathode materials have been the most extensively studied [1].

Na-NiCl$_2$-cathode-based batteries have several advantages over other sodium-beta-alumina batteries, including higher voltage, lower operating temperature, cathode materials with lower corrosive nature, easy assembly, safer discharged-state conditions in case of failure and tolerance against over-charge and over-discharge [2]. For example, the cathode can be charged to a voltage higher than the standard charge thanks to the possibility of partially converting the current collector and the melted NaAlCl$_4$. An evident disadvantage of the Na-NiCl$_2$ battery is the lower energy density, in particular against the Na-S battery. The theoretical specific capacity of Na-NiCl$_2$ ZEBRA batteries is 305 mAh g^{-1}, and the energy density is 788 Wh kg^{-1} (open-circuit voltage at 2.58 V). Despite this impressive theoretical energy density, the real energy density obtained from a conventional tubular Na-NiCl$_2$ battery (operated at ca. 300 °C) is about 95–120 Wh kg^{-1}, a drastic drop due to the additional amount of Ni that is needed to ensure an adequate electrical conductivity through the cathode to improve the battery cycle life.

Although the redox reactions involved in Na-NiCl$_2$ batteries are elementary (see Equation (1)), the mechanisms underlying the processes that lead to cell deterioration are not well understood. The particle growth is the most common phenomenon related to cell degradation. Lu et al. [3] reported several correlations between NaCl/Ni particle growth and battery operating conditions, such as the C-rate, cathode composition and cycling capacity range. High current density, state of charge (SOC) at the end of charge (EOC) and the Ni/NaCl ratio are the main parameters that lead to faster Ni particle growth [4][5]. In the case of NaCl, particle growth closely correlates with the cycling capacity range. Understanding the mechanisms underlying the growth of particles of Ni and NaCl inside the cathode is crucial in order to limit the degradation of the Na-NiCl$_2$ battery. The surface area available for electrochemical reactions is inversely proportional to the particle dimension of active species contained in the cathode. The use of an excess of Ni plays a fundamental role in tolerating the side effects of nickel particle growth. It compensates for the decrease in the surface/volume ratio due to the particle growth. Although the increase in size of both Ni and NaCl can affect the cell's electrochemical performance, NaCl particle growth can be considered a dominant factor. When the cell works within a large cycling capacity range, NaCl particle growth is more evident when the Ni/NaCl ratio decreases. Li et al. [4] reported that NaCl particles larger than 50 μm lead to a significant capacity drop and accelerate the degradation process. Ostwald ripening can explain the growing process of NaCl particles over cycling. This phenomenon is thermodynamically controlled, and the equilibrium is shifted towards the formation of larger particles that are energetically more stable due to a lower surface/volume ratio [6].

Further studies [7] were carried out to understand the charge/discharge processes and improve the performance of nickel chloride cathodes. A low-conducting layer of nickel chloride is formed on the nickel surface during the charging process. Once it reaches a thickness of almost one micrometer, a further charge of the cell is suppressed with a consequent decrease in the utilization factor of the electrode and loss of capacity. The solubility of nickel chloride in the NaAlCl$_4$ melt at elevated temperatures is also important. A fundamental requirement for cathode materials is that their electrochemically active species must be insoluble in melted NaAlCl$_4$ in charged and discharged states. In this way, mass transport of these species to the β″-alumina ceramic surface and their possible exchange with sodium ions in the electrolyte could be avoided [8]. Therefore, the choice of a mixture of components and additives that can mitigate unwanted effects becomes of great scientific interest.

1.1. Sulfur and Sulfide Additives

Oxidation and reduction reactions involving metal sodium at a temperature above its melting point are fast and perfectly reversible processes, which enables high-rate performance at the anode side of the Na-NiCl$_2$ battery. On the other hand, the electrochemical reactions occurring at the positive electrode can remarkably limit the overall battery performance [9]. Bones et al. [10] showed that the Na/NiCl$_2$ cell suffers significant capacity loss even at a low cycling rate due to cathode material. The poor capacity retention during cycling was attributed to the agglomeration of the nickel particles that reduced the surface area and porosity of the nickel electrode. The addition of either sulfur or iron sulfide to the melted NaAlCl$_4$ is typically used to improve the performance of the nickel chloride electrode [5][11]. Indeed, during the electrochemical processes at the cathode, FeS undergoes a fast decomposition to elemental sulfur and polysulfide rather than directly reacting with Ni. This process was found to aid in removing the passivation layer on Ni particles, avoiding an excessive particle growth and improving the cycling behavior of the battery [5]. Furthermore, adding elemental sulfur to the NaAlCl$_4$ electrolyte can prevent particle agglomeration at the electrode surface and effectively improve cycling performance [12]. The mechanisms underlying the improved cycling performance were investigated by Ao et al. [13]. They found that the discharge capacity of a cell without sulfur decreased rapidly as the cycle proceeds, and it retained only 18.6% of the theoretical capacity after 50 cycles. On the other hand, a cell with a sulfur-doped cathode was able to retain a discharge capacity of about 68.6% of the theoretical capacity after 50 cycles. The improved cycle performance was ascribed to a Ni$_3$S$_2$ layer formed on the nickel particles, which enhances the blocking effect by a self-repairing function of Ni$_3$S$_2$ on the particle surface when an optimal amount of sulfur is used.

Sulfur was also proposed as the main constituent for mixed Ni, NaCl and Na$_2$S cathode composition [14]. The resulting hybrid Na-S and Na-NiCl$_2$ battery showed a 50% increase in energy density over ZEBRA batteries and stable cycling with more than 95% of cell capacity retained over 60 cycles. In this cathode mixture, polysulfide species could participate in the electrochemical reactions during discharge, leading to a higher theoretical energy density than the traditional Na-S or Na-NiCl$_2$ batteries.

1.2. Sodium Iodide and Bromide Additives

Prakash et al. [8][15] showed that adding sodium iodide (NaI), sodium bromide (NaBr) and sulfur additives in the cathode mixture significantly increased the capacity and reduced the impedance of the Na/NiCl$_2$ cells, leading to higher nickel utilization. In particular, they found that a NaI additive enhances the performance of the nickel chloride electrode by two different mechanisms. The first one, involving the doping of the solid NiCl$_2$, is dominant at potentials lower than the potential of iodine evolution (~2.8 V vs. Na), producing higher capacity and lower impedance on the cathode. The second benefit occurs when the cell cycles through the iodine evolution potential range (2.8–3.1 V). In this case, the presence of dissolved iodine species improves the mass transport through the liquid phase, and thus the electrode kinetics.

Li et al. investigated different alkali metal salts, such as NaBr, LiCl and LiBr, as potential additives for the cathode of a Na-NiCl$_2$ battery [16]. They showed that a partial replacement of NaCl with these alkali metal salts improves the ionic conductivity of the secondary electrolyte. This improvement was attributed to their lower bond polarity and more irregular structures, allowing easier ion mobility that determines a lower melting temperature. The positive effects of NaCl replacement on the ionic conductivity was more evident at 150 °C, the temperature at which NaAlCl$_4$ is in a solid state. In fact, the melting temperature of molten salts is related to the strength of their ionic bond. For example, NaBr (T$_m$ = 747 °C) has a lower melting temperature than NaCl (T$_m$ = 801 °C) since NaBr has weaker ionic bond strength due to the larger ionic radius of Br$^-$ compared to Cl$^-$. A Na/NiCl$_2$ cell with 50 mol% of NaBr exhibited reduced polarizations and stable performance at 150 °C, a temperature that is significantly lower than the normal ZEBRA battery operating temperature. These findings suggest the use of a low-melting-point ternary catholyte as a feasible solution for the development of intermediate-temperature Na/NiCl$_2$ batteries.

2. Alternative Cathode Formulations

The Ni content in the cathode accounts for more than 60% of the total cost of a Na-NiCl$_2$ battery. The amount of nickel in the cathode mixture needs to be more than three times higher with respect to the stoichiometric ratio for the electrochemical reaction. Therefore, reducing the Ni amount by increasing its utilization factor is one of the main open challenges [17]. However, it is well known that Ni/NaCl ratios lower than 1.8 lead to fast battery degradation at an operating temperature of 280 °C [4]. For instance, to reduce the Ni content, Chang et al. [18] investigated several cathodes with different Ni/NaCl ratios (i.e., 1.8, 1.5, 1.25, 1.0 and 0.75). They found that a cell with a Ni/NaCl ratio of 1.25 showed the highest specific energy density of 405 Wh kg^{-1}, i.e., a 16% increase over that of the Ni/NaCl ratio at 1.8. Moreover, this cathode requires 15% less Ni, which reduces the total Ni cost by as much as 30%. Long-term cycling testing also

demonstrated that the cell with a Ni/NaCl ratio of 1.25 is incredibly stable over 300 cycles, showing no significant cathode particle growth after cycling.

However, different cathode chemistries could be used as alternatives to standard Ni/NaCl. Among these, the sodium-iron chloride (Na-FeCl$_2$) redox couple represents the most promising candidate. The first ZEBRA battery ever built was based on this cathode formulation, although, due to the lower performance and poor stability, it was soon replaced by the current Na-NiCl$_2$ battery [19]. Nevertheless, due to the low cost of the raw material, interest in batteries with an iron-based cathode has been revived. In this regard, a PNNL research group presented an advanced Na-FeCl$_2$ battery, which, in addition to a high energy density, was able to operate at intermediate temperatures below 200 °C with excellent cyclic stability [20][21]. In particular, they demonstrated that the discharge capacity of a typical Na-FeCl$_2$ cell after ten conditioning cycles was about 150 mAh g^{-1}, equivalent to 93% of its theoretical capacity (160.9 mAh g^{-1}), based on the NaCl content in the cathode. The extra capacity beyond the theoretical value, observed for the first conditioning cycle, originated from other sodium sources such as Na$_2$S/S, initially added into the cathode to activate the Fe surface. At 190 °C, the cell delivered a specific capacity of ≈116 mAh g^{-1} (74% of the total) at a notably high current density of 33.3 mA cm^{-2} (≈0.6 C). However, it was demonstrated that Fe particle pulverization and the subsequent loss of the electron-conduction network are the primary causes of capacity fading during the long-term cycling of Na-FeCl$_2$ cells. To mitigate this effect, a small amount of Ni additive (10 wt%) was introduced into the Fe/NaCl cathode. This specific cathode formulation achieved excellent cycling stability, maintaining a discharge energy density of over 295 Wh kg^{-1} for 200 cycles at a current rate of about C/5.

Instead of the full iron-based cathode, sodium-nickel/iron chloride Na-(Ni, Fe)Cl$_2$ cells have been more intensively studied to reduce the amount of expensive Ni in a standard Na-NiCl$_2$ battery. Ahn et al. [22][23][24] prepared different mixtures of Ni and Fe and investigated the effect of composition and cathode microstructure on battery performance. They demonstrated that the use of larger iron particles and smaller nickel particles leads to a well-connected microstructure in which the active metallic Ni acts as a conductive path for the rapid mobility of electrons in the cathode. In addition, the thickness of the NiCl$_2$ layer formed on Ni particles could be reduced, further improving the electron transfer kinetic. Using an optimized size ratio between Fe and Ni particles, up to 50% of the Ni content was successfully replaced, obtaining at the same time excellent cell capacity and cycle performance. A similar study was also carried out by Frusteri et al. [25]. They found that, although Ni, Fe and NaCl microstructures are not finely designed, the cathode composition plays a crucial role in the electrochemical performance of the cell. In particular, by increasing the amount of Fe particles in the cathode composition, up to an optimal 0.5/0.5 Ni/Fe ratio, the specific capacity of the Na-(Ni, Fe)Cl$_2$ cell can be improved.

As an alternative to the two most common halides, NiCl$_2$ and FeCl$_2$, other metal halides could be promising candidates for high-temperature sodium batteries. Among these, aluminum (Al), an earth-abundant and inexpensive metal, has been recently considered. For instance, Xue et al. [26] proposed a Na-NaAl$_2$Cl$_7$-NaAlCl$_4$ battery operating at 200 °C with a molten sodium anode, a combined acidic–basic NaAl$_2$Cl$_7$-NaAlCl$_4$ catholyte, and a Na$_3$Zr$_2$Si$_2$PO$_{12}$ (NaSICON) solid electrolyte as the separator. They reported a high energy density of 366 Wh kg^{-1} with an output voltage of 1.55 V. During cell operation, the deposition and dissolution of NaCl and Al were found to govern the cathode reaction. The use of a high-surface-area cathode electrode was the key to achieve full capacity. Moreover, the cell assembly in the discharged state without the handling of metallic Na was shown. Zahn et al. [27] also proposed a similar Na-Al battery using a NaAlCl$_4$ catholyte and β″-alumina as a solid electrolyte. The battery presented a stable coulombic efficiency of 100% and an energy efficiency of about 95%. The cell also maintained an excellent capacity retention of 97.6% after 200 cycles at a current rate of C/3.

Another promising active material for metal halide sodium batteries is zinc (Zn). Due to a market value of about 10% of the Ni cost, replacing Ni with Zn in the Na-NiCl$_2$ cathode can cut the overall battery price [28]. A sodium-zinc chloride (Na-ZnCl$_2$) cell operating at a temperature higher than 250 °C, and later also investigated at an intermediate temperature of 190 °C, was proposed by Lu et al. [29][30]. They demonstrated that the performance of Na-ZnCl$_2$ was similar to that of a Na-NiCl$_2$ cell operating at the same conditions. For example, the capacities for the Na-ZnCl$_2$ and Na-NiCl$_2$ cells were 110 and 102 mAh at a current of 60 mA, respectively. Moreover, the performance of the Na-ZnCl$_2$ cell at higher charging/discharging rates was superior to that of the Na-NiCl$_2$ cell.

Although copper is more expensive than aluminum and zinc, this metal has also been proposed as a promising candidate in the production of cathodes for sodium-metal halide batteries [31][32][33]. The main reasons are that it has a larger abundance than nickel and that there is high potential for the CuCl$_2$/Cu redox couple of 2.74 V in Na-based battery systems [34]. Niu et al. [35][36] showed that sodium-copper chloride (Na-CuCl$_2$) batteries are able to be charged/discharged at operating temperatures down to 100 °C. This was obtained by replacing the traditional NaCl-saturated NaAlCl$_4$ with an ionic catholyte liquid at room temperature. According to the different ionic liquids and their compositions, the fabricated cells delivered a specific capacity higher than 141 mAh g^{-1} at 175 °C, even though 92% of the initial capacity was

retained only within 20–50 cycles. Moreover, with the optimal composition of the catholyte, the battery could run at 130 °C, even showing a reversible capacity of 79.2 mAh g^{-1} when the operating temperature was set at 100 °C.

One of the most recent challenges is the fabrication of electrodes containing a continuous conductive network that is stable during charge and discharge processes. A conductive network of evenly dispersed nickel mixed with other inert conductive materials could be a valuable solution. In this regard, carbon-metal halide hybrid materials have been proposed to improve the activity of the cathode and the overall rate performance of the sodium-metal halide batteries. Chang et al. [17] tested a nickel-coated graphite core–shell microarchitecture to replace pure Ni powders.

This particular structure takes advantage of the electrically conducting graphite core that provides a stable electron-percolating pathway within the cathode, with minimum Ni content. The nickel–carbon microstructure conferred to the cell an excellent initial energy density of 133 Wh kg^{-1} (at ~C/4) and an energy efficiency of 94% at an intermediate temperature of 190 °C. Moreover, the Ni loading in the cathode was reduced by 40% compared to conventional Na-NiCl$_2$ batteries. Although a partial delamination of Ni layers from graphite particles during cycling was observed at 280 °C, battery degradation could be mitigated operating at 190 °C, with stable performance up to 150 cycles.

The electrospinning technique can also effectively produce a continuous conductive carbon fiber network to improve the rate performance of Na-NiCl$_2$ batteries. Gao et al. [37] investigated a nickel–carbon composite synthesized by the electrospinning method, followed by an annealing in an inert atmosphere. The composite was made of electrochemically active nickel nanoparticles well dispersed in inert carbon nanofibers, which played the role of a continuous conductive network. The cell based on the composite nanofiber cathode retained 80% of the initial capacity at 0.3 C after 400 cycles and maintained a coulombic efficiency of around 100%. At a high current rate over 2 C, the composite cathode was able to work more than 350 cycles without obvious degradation. The blocking effect of the carbon fibers, restricting the volume expansions of Ni and NaCl particles, limited the growth of grains over cycles.

In order to improve the performance of the NiCl$_2$ cathode, the use of a conductive network incorporating carbon nanostructures was also investigated. Li et al. [38] proposed a hybrid aerogel of NiCl$_2$-rGO. Graphene aerogel is often selected as a 3D carbon matrix to fabricate graphene-based composite electrodes for energy storage applications due to its excellent high specific surface area, electrical conductivity and strong stability. The NiCl$_2$-rGO aerogel exhibited a charge capacity of 128.1 mAh g^{-1} and a discharge capacity of 116.6 mAh g^{-1} after 50 cycles. The performance of the NiCl$_2$-rGO aerogel was attributed to the excellent conductivity of rGO and the strong contact between NiCl$_2$ and graphene sheets. However, NiCl$_2$ is totally transformed into Ni and NaCl particles on the surface of graphene sheets after the first discharge. Therefore, part of the Ni and NaCl particles may detach from the rGO matrix, resulting in an uneven load of NiCl$_2$ on graphene sheets and a rapid loss of Ni/NaCl during subsequent cycles. Li et al. [39] also proposed an advanced free-standing Ni-less cathode with Ni/NaCl particles uniformly distributed in a conductive matrix consisting of a 3D hierarchical structure made by carbon fibers (CFs) and multi-walled carbon nanotubes (MWCNTs). The MWCNTs and CFs, in addition to offering enough void space to accommodate the growth of NaCl particles, can provide excellent electron pathways around Ni particles and thus avoid an excess of Ni. The cell assembled with a Ni-less cathode could operate at 190 °C, also delivering a high energy density of 263 Wh Kg^{-1} after 170 cycles.

Table 1 shows a summary of the main performance, such as operating temperature, c-rate, energy density and efficiency of the above-discussed cathode formulations used for the realization of high- and intermediate-temperature sodium-metal halide cells.

Table 1. Main performance of the most representative cathode materials.

Sample	Temp (°C)	C/Rate	Energy Density (Wh/kg)	Energy Efficiency (%)	Reference
Ni/NaCl ratio 1.8	280	C/3	~150	96	[4]
Ni/NaCl ratio 1.0	190	C/5	285	60	[18]
Ni/NaCl ratio 1.25	190	C/5	330	96	[18]
Ni/NaCl ratio 1.5	190	C/5	390	98	[18]
Ni/NaCl ratio 1.8	190	C/5	420	98	[18]
Na (10µm)/NaCl (50 µm)	280	C/5	~250	92	[3]
Na (1µm)/NaCl (5 µm)	190	C/5	340	88	[3]

Sample	Temp (°C)	C/Rate	Energy Density (Wh/kg)	Energy Efficiency (%)	Reference
Na-S NiCl$_2$ hybrid	280	C/5	248	90	[14]
Na-FeCl$_2$	190	C/8	135	92	[20]
Ni-Fe/NaCl (ratio Ni-Fe 1:1)	300	C/5	275	91	[25]
NaAl$_2$Cl$_7$–NaAlCl$_4$	200	C/10	366	96	[26]
Na-Al/NaAlCl$_4$	190	C/3	447	95	[27]
Na-ZnCl$_2$	280	-	~225	-	[29]
Na-CuCl$_2$	175	-	~388	-	[36]
Na-NCG	190	C/4	133	94	[17]
MWCNT/CF/Ni/NaCl	190	-	263	-	[39]

3. Effect of Temperature

One of the main challenges for sodium-metal halide batteries is lowering the operating temperature to reduce cell degradation, thereby improving their cycle life. However, operation at intermediate temperatures below 200 °C can cause various limitations to battery performance.

Hosseinifar et al. [40] performed several tests at the extremes of the common temperature range employing an aggravated charge–discharge regime of a Na-NiCl$_2$ battery. The cells cycled with a charging voltage of 3.1 V per cell underwent a noticeable degradation at 260 °C and 350 °C. The cells cycled at 260 °C showed, in discharge mode, low resistance for 300 cycles and a subsequent rapid failure. In particular, this occurred after a few cycles in which cells were slightly over-charged. The worsening of the charge and discharge behavior at 260 °C was ascribed to a high-resistance layer formed close to the solid electrolyte. This layer was identified as AlF$_3$ particles deposited on the surface of beta-alumina. The cells cycled at 350 °C did not fail as observed at 260 °C. AlF$_3$ was only seen in the form of coarse particles. Nonetheless, these cells showed high internal resistance and severe capacity loss by the end of cycling and underwent deep over-charges. The growth of Ni particles was attributed to the capacity loss in the cells cycled at 350 °C. The combination of high temperature, NiCl$_2$ dissolution in the molten electrolyte and the formation of the Ni$_3$S$_2$ phase was believed to be responsible for the Ni grain growth in the high-temperature-operating cells.

On the other hand, the operation at temperatures as low as 240 °C can be relatively feasible and advantageous for the general Na-NiCl$_2$ battery efficiency. Gerovasili et al. investigated the performance of an 80 Ah commercial Na-NiCl$_2$ battery below usual operating temperatures [41]. The total available capacity measured at 240 °C and at 0.1 C was only 1.8% lower than in normal operating conditions, such as 275 °C and 310 °C. However, operating at the quickest charge rate, around 25 h was required to achieve a full charge from a 20% SOC, while for a charge from a 20% to 90% SOC, the time for charging was reduced to 7.6 h. At this SOC window, the total daily efficiency was always higher at 240 °C when the discharge current ranged from 0.125 C to 0.25 C, even though the cycle efficiency was slightly lower or the same at 240 °C compared to 275 °C. However, they concluded that lower heat losses at 240 °C could result in up to a 49% reduction in heating energy compared with operation at 275 °C.

Lu et al. [42] also investigated the effect of temperature on planar-type Na/NiCl$_2$ batteries, observing a significant influence on the stability of cell performance during cycles. They showed that a higher operating temperature resulted in a more rapid increase in cell polarization with cycling. In particular, a 55% increase at the end of charge polarization was observed at 280 °C after 60 cycles, while little change was found in the cell tested at 175 °C. The performance degradation at higher temperatures was attributed to the particle growth of both nickel and sodium chloride in the cathode. They concluded that cell operation below 200 °C is feasible and provides better stability.

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