An Intermediate-Temperature High-Performance Na–ZnCl₂ Battery

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ABSTRACT: The Na–β-alumina battery (NBB) is one of the most promising energy storage technologies for integrating renewable energy resources into the grid. In the family of NBBs, Na–NiCl₂ battery has been extensively studied during the past decade because it has a lower operating temperature, better safety, and good battery performance. One of the major issues with the Na–NiCl₂ battery is material cost, which is primarily from Ni in the battery cathode. As an alternative, Zn is much cheaper than Ni, and replacing Ni with Zn in the cathode can significantly reduce the cost. In this work, we investigate the performance and reaction mechanism for a Na–ZnCl₂ battery at 190 °C. Two-step reversible reactions are identified. During the first step of charging, NaCl reacts with Zn to produce a ribbon-type Na₂ZnCl₄ layer. This layer is formed at the NaCl–Zn interface rather than covering the surface of the Zn particles, which leads to an excellent cell rate capability. During the second step, the produced Na₂ZnCl₄ is gradually consumed to form ZnCl₂ on the surface of Zn particles. The formed ZnCl₂ covers most of the surface area of the Zn particles and shows a limited rate capability compared to that of the first step. We conclude that this limited performance of the second step is due to the passivation of Zn particles by ZnCl₂, which blocks the electron pathway of the NaCl–Zn cathodes.

INTRODUCTION

Electrochemical energy storage systems or rechargeable batteries have gained increasing attention for both stationary and transportation applications during the past two decades. Among various types of storage technologies, Na–β-alumina batteries (NBBs) based on a β'-Al₂O₃ solid electrolyte (BASE) and a molten sodium anode have been widely studied. There are two main types of NBBs based on the particular cathode materials. One is the sodium–sulfur (Na–S) battery with molten sulfur/polysulfides as the cathode material. The other one is sodium–metal halide (Na–MH or ZEBRA) batteries, in which a solid transition metal halide (e.g., NiCl₂ or FeCl₂) is used in the cathode. A secondary molten electrolyte of NaAlCl₄ (melting point of 157 °C) is typically employed in the Na–MH batteries. The molten electrolyte primarily serves as a sodium ion transport medium between the BASE and the reaction zone in the cathode and does not participate in the electrochemical reactions.

In conventional Na–MH batteries, one critical requirement for the cathode material is that electrochemically active species in the cathode must be insoluble in the NaAlCl₄ melt. Therefore, mass transport of the species to the BASE surface and the subsequent ion exchange with sodium in the BASE could be prevented. Among all transition metal halides, NiCl₂ has been extensively studied primarily because it offers simple cell reactions, good cell voltage, and lower solubility in the NaAlCl₄ melt. For example, with additives such as sodium bromide, sodium iodide, and sulfur, the solubility of NiCl₂ in the melt can be reduced to the parts per million level at temperatures of ~300 °C, which can effectively hinder the ion exchange of Ni²⁺ with Na⁺ in the BASE and extend battery cycle life. Aside from these benefits, one of the major issues with the Na–NiCl₂ battery is material cost. According to our previous study, cell material represents 39% of the overall battery cost, and 63% of the cell material cost comes from Ni metal. So, the cost of Ni metal is ~25% of the overall battery cost.

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Replacing Ni with other low-cost metals, such as Fe or Zn, would significantly reduce the battery cost. For example, the cost of Zn is ∼10% of that of Ni. Owing to the lower material cost, various Zn-based rechargeable batteries, including Zn/MnO₂ batteries in mild aqueous and alkaline solutions, Zn/Prussian blue analogue batteries, Zn/I₂ batteries, and Zn-ion intercalating anode battery have been extensively studied for stationary energy storage applications. Based on our calculation, replacing Ni with Zn in the Na−NiCl₂ cathode can cut around 46 and 20% of the cell material and overall battery costs, respectively. Recently, our group has expended a lot of effort to explore the possibility of using Fe or Zn to replace Ni in the cathode. We demonstrated that a Na−FeCl₂ battery can be assembled in a discharged state by adding sulfur-based additives to the cathode. It was found that the polysulfide species generated in situ during the initial charging process can activate the Fe cathode via removing the passivation oxide layers on the surface of Fe powders.

For the Na−ZnCl₂ system, we have successfully demonstrated cell performance at temperatures of 240 and 280 °C. Here, we further investigated its performance at a reduced temperature of 190 °C. Reducing the temperature below 200 °C is meaningful for Na−MH batteries because it could significantly improve the battery durability and safety and allow cost-effective materials for the battery components (e.g., sealing and casing) and battery manufacturing/maintenance, which eventually will lower the overall cost of the battery system. In this study, the relationship between cell performance (e.g., capacity and rate capability), cathode microstructure (e.g., particle size, morphology, and distribution), and electrochemical reactions was thoroughly evaluated at the reduced operating temperature. The performance of Na−ZnCl₂ cells is also compared with that of Na−NiCl₂ cells. On the basis of the observed results, cathode reaction mechanisms for the Na−ZnCl₂ cell are proposed at the end of this study.

RESULTS AND DISCUSSION

Figure 1a shows the performance of a Na−ZnCl₂ cell at 190 °C compared with that of a Na−NiCl₂ cell under similar conditions. For the Na−ZnCl₂ cell, two steps with two plateaus were observed in the voltage profile, which was similar to those at the operating temperature of 240 °C. A phase diagram between NaCl and ZnCl₂ is shown in Figure 1b. Three different solid phases appear in the phase diagram at 190 °C, including NaCl, Na₂ZnCl₄ (at a ZnCl₂ mole fraction of 0.33), and solid ZnCl₂. Accordingly, the phase diagram can be divided into two different regions: (i) ZnCl₂ mole fraction of 0 to 0.33, NaCl + Na₂ZnCl₂; and (ii) ZnCl₂ mole fraction of 0.33 to 1, Na₂ZnCl₂ + ZnCl₂, which appeared as the two plateaus in the cell charging/discharging curve in Figure 1a. Similar to our previous study, two reversible electrochemical reactions were proposed in conjunction with the two steps (two plateaus):

Step 1: 4NaCl + Zn ⇌ Na₂ZnCl₄ + 2Na Cl₂ + ZnCl₂

E = 1.94 V

Step 2: Na₂ZnCl₄ + Zn ⇌ 2ZnCl₂ + 2Na Cl₂ + Zn

E = 2.13 V

To confirm the formation of these phases during the electrochemical reactions, XRD analysis was carried out for the cathodes of four cells in which charging was stopped at 0, 25, 50, and 100% states of charges (SOCs; see the arrows in Figure 1a). Figure 2 shows the XRD patterns for these cathodes. As
shown in Figure 2a, the peaks from NaCl, Ni, and NaAlCl₄ were observed in the cathode at 0% SOC. At 25% SOC, Na₂ZnCl₄ was detected, and the existence of Na₂ZnCl₄ and absence of ZnCl₂ confirmed that Na₂ZnCl₄, rather than ZnCl₂, formed during this stage of charging (step 1). At 50% SOC, however, the peaks from NaCl disappeared, indicating that all of the active NaCl has been converted to Na₂ZnCl₄ and the active materials in the cathode were Na₂ZnCl₄ and Zn at this point. After 50% SOC, the Na₂ZnCl₄ was gradually consumed with the production of ZnCl₂, and the final products in the cathode consisted of ZnCl₂ and Zn. It should be noted that an excessive amount of Zn is typically incorporated into the battery cathode as electron percolation paths, which can ensure sufficient electrical conductivity throughout the charging/discharging processes. It can explain why the intensity of Zn metal peaks was so strong even at the end of charge, as seen in Figure 2d. According to the abovementioned two electrochemical reactions, the NaCl utilization rates at the end of each step were 50 and 100%, respectively, which exactly matched the steps appearing in the charging/discharging curve in Figure 1a.

To test the rate capability, the Na−ZnCl₂ cell was operated at different charging/discharging rates. The performance of the cell was also compared with that of the Na−NiCl₂ cell as shown in Figure 3a. At a charging/discharging current of 20 mA, the capacities of the Na−ZnCl₂ cell were similar to those of Na−NiCl₂ cells (i.e., ~149 mAh). With the increase of the charging/discharging rate, the capacities for both cells decreased significantly. However, the capacity retention of the Na−ZnCl₂ cell was significantly higher. For example, the capacities for the Na−ZnCl₂ and Na−NiCl₂ cells were 110 and 102 mAh at a current of 60 mA, respectively. At a current of 100 mA, the retentions were 61 (96 mAh) and 41% (64 mAh) for the Na−ZnCl₂ and Na−NiCl₂ cells, respectively. Apparently, the performance of the Na−ZnCl₂ cell at higher charging/discharging rates was superior to that of the Na−NiCl₂ cell. To investigate the mechanism responsible for the superior performance of the Na−ZnCl₂ cell at higher charging/discharging rates, the voltage profiles of the cell at different rates were compared as shown in Figures 3b-d.

Figure 3. (a) Charge/discharge capacity of Na−ZnCl₂ and Na−NiCl₂ cells at different charging/discharging rates. Voltage profiles of the two cells at constant currents of (b) 20, (c) 60, and (d) 100 mA. (e) Comparison of capacity retention between the Na−ZnCl₂ and Na−NiCl₂ cells.
currents were compared with those of the Na–NiCl₂ cell in Figure 3b–d. As shown in Figure 3b, at a constant current of 20 mA, the capacities of Na–NiCl₂ were ~94% of the theoretical one. For the Na–ZnCl₂ cell, they were around 96% of the theoretical one, with 46% of the capacities from step 1 and the other 50% from step 2. When the current was increased to 60 mA, the capacities of the Na–NiCl₂ cell were 65% of the theoretical value, whereas they were 42 and 28% for the first and second steps in the Na–ZnCl₂ cell, respectively. At a constant current of 100 mA, the Na–NiCl₂ cell retained 41% of the theoretical capacity, and the capacities were 38 and 23% for the Na–ZnCl₂ cell. These results along with the capacities at other currents are summarized in Figure 3e. For the Na–ZnCl₂ cell, the capacity retention rates for steps 1 and 2 were close to each other at a low current of 20 mA, which was also very similar to that of the Na–NiCl₂ cell. However, the retention rate (~0.11 in slope) for step 1 was significantly higher than that of step 2 (~0.34 in slope) at the higher currents. The major difference between the two steps is the reaction product (i.e., Na₂ZnCl₄ vs ZnCl₂). Thus, we believe that the higher rate capability for step 1 was related to the formation of Na₂ZnCl₄. More discussions will be presented with other characterization techniques (e.g., electrochemical impedance spectroscopy and scanning electron microscopy (SEM)) in the following section.

Figure 4 shows the impedance spectra of the Na–ZnCl₂ cells stopped at different SOCs at (a) 0, (b) 25, (c) 50, and (d) 100%. (e) Equivalent circuit employed for the impedance spectra fitting.

Table 1. Parameters Calculated from the Fitting Model for the Na–ZnCl₂ Cells at Different SOCs

| SOC    | R₁ (Ω)  | R₂ (Ω)  | CPE-T (×10⁻³) | CPE-P  |
|--------|---------|---------|---------------|--------|
| 0% SOC | 0.88    | 0.17    | 2.2           | 0.44   |
| 25% SOC| 1.02    | 0.18    | 8.0           | 0.55   |
| 50% SOC| 1.23    | 0.24    | 1.6           | 0.6    |
| 100% SOC| 1.48    | 0.48    | 3.7           | 0.71   |

increased with the increase of SOC. This was reasonable because Zn particles serve as the electron pathway in the cathode and they were continuously consumed during charging, which led to the increase in the cathode and overall cell ohmic resistance. Although the value of R₂ slightly increased from 0 to 50% SOC, it doubled from 50 to 100% SOC. R₂ is the charge-transfer resistance, which was mainly from the cathode. The much lower R₂ values during testing at 0 and 50% SOC (step 1) were in agreement with their higher capacity and rate capability, as shown in Figure 3.

To further understand the mechanism for the higher capacity and rate capability, the microstructures of the NaCl–Zn cathodes at different SOCs were analyzed using SEM/energy-dispersive X-ray (EDX) spectroscopy. The cross-sectional images and EDX maps of the cathodes are shown in...
Figure 5. Figure 5a shows the SEM image of the cathode at 0% SOC. According to the XRD results, the cathode consisted of NaCl and Zn along with NaAlCl₄. The bright particles with irregular shapes were Zn metal, which was confirmed by EDX elemental mapping (Figure 5b). It should be noted that, because the position of the Lα emission line from elemental Zn is very close to that of the Kα emission line from elemental Na (1.012 vs 1.041 keV), the signals from Zn metal were observed in the Na elemental mapping (see Figure 5c). However, as shown in the figure, the signals from Zn were stronger than those from Na, so we still could differentiate Zn metal from NaCl. The slightly bright red particles were Zn metal, whereas the dark ones were NaCl with an average size of ∼10 μm. The existence of NaCl particles was also confirmed from Cl mapping, as shown in Figure 5d (bright yellow spots). After the combined analysis of Figure 5b–d, we confirmed that the other areas with a medium yellow color in Figure 5d were NaAlCl₄. On the basis of the discussion above, we can conclude that, at the beginning of charging (0% SOC), the cathode consisted of Zn metal and NaCl. The NaCl particles were round with an average size of ∼10 μm. Figure 5e shows the SEM image of the cathode at 50% SOC. The morphology of the cathode was different from that at 0% SOC (see Figure 5a). Ribbons with a width of 5–10 μm were observed in the microstructure. After carefully analyzing the elemental maps in Figure 5f–h, we believed that the ribbons were Na₂ZnCl₄, and the irregularly shaped particles with a brighter color in Figure 5g were Zn metal; the round NaCl particles disappeared. These were consistent with the XRD results, indicating that all of the active NaCl was converted to Na₂ZnCl₄, and the active materials in the cathode were Na₂ZnCl₄ and Zn metal at 50% SOC. Figure 5i–l shows the cross-sectional images and EDX maps of the cathode at 100% SOC. The cathode morphology was completely different from those at 0 and 50% SOCs. The ribbon-type Na₂ZnCl₄ disappeared, and ZnCl₂ formed at the edge of the Zn particles. At the end of charging, ZnCl₂ was the final product along with excess Zn particles as the electron percolation pathway.

On the basis of all the results and discussion above, we have proposed a reaction mechanism for the Na−ZnCl₂ chemistry at 190 °C. The mechanism is similar to that of the well-known mechanism for the Na−NiCl₂ system proposed in our previous study.13 Two mechanisms are compared in Figure 6. For the Na−NiCl₂ system, the active materials in the cathode are NaCl and Ni before charging (refer to Figure 5a). The particle size of NaCl is significantly larger than that of Ni on the basis of our previous observation. At the beginning of charging, NaCl reacts with Ni to form NiCl₂ in the contact area of the two particles, as shown in Figure 6a. The formation of a NiCl₂ layer at the interface isolates Ni from NaCl, which limits further reaction between the two particles. Then, during the continued charging, Ni particles react with NaCl in the NaAlCl₄ melt, which forms NiCl₂ layers on the surface of Ni. To maintain neutrality of the melt, the NaCl particles continuously dissolve into the melt. At the end of charging, all of the active NaCl is

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Figure 6. Cathode reaction mechanisms for (a) Na−NiCl₂ and (b) Na−ZnCl₂ batteries.
consumed, and a thick layer of NiCl$_2$ covers most of the surface of the Ni particles. Because NiCl$_2$ is nonconductive, this coating significantly limits the rate capability for the Na–NiCl$_2$ cell, as shown in Figure 3a,e. A two-step reaction mechanism is proposed for the Na–ZnCl$_2$ system, which is unlike the Na–NiCl$_2$ counterpart. During step 1, NaCl reacts with Zn to form a thin layer of Na$_2$ZnCl$_4$ in the contact area of the two particles (refer to Figure 6b), which is similar to the Na–NiCl$_2$ counterpart. The major difference is that, unlike NiCl$_2$, the formed Na$_2$ZnCl$_4$ layer likely serves as a bridge and can continuously supply either NaCl or Zn$^{2+}$ to the reaction sites, which finally consumes all of the active NaCl and forms a ribbon-type Na$_2$ZnCl$_4$ layer at the end of the step (i.e., middle of charging), which was confirmed by the SEM images (refer to Figure 5e). Because the Na$_2$ZnCl$_4$ layer is only formed at the interface of the particles rather than covering most of the surface area of the Ni particles, the rate capability for this step is not affected, as shown in Figure 3a,e. During step 2, the formed Na$_2$ZnCl$_4$ is gradually consumed to form a thin layer of ZnCl$_2$ at the interface. Similar to that with NiCl$_2$, the formation of the ZnCl$_2$ layer isolates Zn from Na$_2$ZnCl$_4$, which prohibits further reaction between the two particles. The continued charging is through the NaAlCl$_4$ melt, which forms ZnCl$_2$ layers on the surface of Zn. The nature of ZnCl$_2$ is similar to that of NiCl$_2$, so the formed ZnCl$_2$ covers most of the surface area of the Zn particles and leads to a limitation in the rate capability as well.

**CONCLUSIONS**

The cathode reaction mechanism for the Na–ZnCl$_2$ battery has been investigated at 190 °C. Two-step reversible reactions have been identified. During charging, a first-step reaction between NaCl and Zn particles generated Na$_2$ZnCl$_4$ at the interface. The produced Na$_2$ZnCl$_4$ served as a bridge and continuously supplied either NaCl or Zn$^{2+}$ to the reaction sites, which finally formed a ribbon-type Na$_2$ZnCl$_4$ layer at the interface of the particles. Because the Na$_2$ZnCl$_4$ layer was formed at the interface rather than covering the surface of the Ni particles, the rate capability for this step was excellent. During step 2, the formed Na$_2$ZnCl$_4$ was gradually consumed to form ZnCl$_2$ at the interface between Na$_2$ZnCl$_4$ and Zn. The formation of the ZnCl$_2$ layer isolated Zn from Na$_2$ZnCl$_4$, which prohibited further reaction between the two phases. The continued charging was through the NaAlCl$_4$ melt, which formed ZnCl$_2$ layers on the surface of Zn particles. Because of the nonconductive nature of ZnCl$_2$, the formed ZnCl$_2$ covered most of the surface area of Zn particles, which led to a limitation in the rate capability.

**EXPERIMENTAL**

**Fabrication of BASE Discs.** BASE discs were fabricated using a vapor phase process, as described previously. Starting powders were high-purity α-Al$_2$O$_3$ (Almatis, >99.8%) and yttria-stabilized zirconia (YSZ, UCM Advanced Ceramics, 8 wt %). A mixture of 70 vol % α-Al$_2$O$_3$ and 30 vol % YSZ was ball-milled with a dispersant (Phospholan PS-236, AkzoNobel), solvents (methyl ethyl ketone/ethanol), a plasticizer (benzyl butyl phthalate, Aldrich), and a binder (Butvar B-79) to make a slurry. After the slurry was cast into a thin sheet (∼125 μm), the sheets were laminated and laser-cut to form discs. The discs were sintered at 1600 °C in air to achieve full density (>99%). The sintered α-Al$_2$O$_3$/YSZ discs were then placed in loose β″-Al$_2$O$_3$ powder with 10% NaAlO$_2$ and heat-treated at 1450 °C in air to convert α-Al$_2$O$_3$ into β″-Al$_2$O$_3$. The β″-Al$_2$O$_3$ powder used in the conversion process was synthesized using boehmite, Na$_2$CO$_3$, and Li$_2$CO$_3$ via a solid-state reaction. The conversion occurred by a coupled transport of sodium and oxygen ions from the β″-Al$_2$O$_3$ powder to the samples. The thickness of the converted composite β″-Al$_2$O$_3$/YSZ discs was ∼500 μm.

**Cell Construction and Testing.** During cell testing, the cell cathode consisted of granules of Zn or Ni, NaCl, and small amounts of additives. The molar ratio between metal (i.e., Zn or Ni) and NaCl in the cathode was 1.8:1. An amount of Zn metal (∼28%) was consumed during the electrochemical reactions, and the rest of the Zn metal (∼72%) was for electron percolation. The Ni particles were round with a particle size of 2–10 μm, and the Zn particles were irregular with a size from 5 to 30 μm. After a final drying treatment to eliminate all traces of moisture under vacuum at 200 °C, molten NaAlCl$_4$ secondary electrolyte was infiltrated into the granules. A foil and a spring made of Mo were placed on top of the cathode as the current collector. On the anode side, a spring-loaded metal shim was inserted into the anode compartment to serve as a sodium reservoir. The anode and cathode end plates were then compressed onto the α-Al$_2$O$_3$ ring with metal O-rings. Nickel leads were welded to the electrode end plates as current collectors. The active cell area was ∼3 cm$^2$.

The assembled cells were heated in air to 190 °C for testing. For Na–ZnCl$_2$ cells, they were initially charged up to 2.3 V with a constant current of 10 mA (i.e., 3.33 mA/cm$^2$). The cells were then discharged back to 1.7 V under the same current. After the initial cycle, the cells were cycled between the cutoff voltages of 1.7 and 2.3 V. For those cells cycled at higher current densities (>20 mA/cm$^2$), the cutoff voltages were 1.7 and 2.4 V to ensure reasonable cell performance. The Na–NiCl$_2$ cells were cycled between 1.8 and 2.8 V. The cycling was under constant currents from 6.67 to 33.33 mA/cm$^2$ for both charging and discharging.

**Post-analysis of the Cathode.** After cell testing, a few of the cells were stopped at different states of charge (SOCs), and the impedance spectra were collected with an electrochemical interface (Solartron 1287, Solartron Analytical) and a frequency response analyzer (Solartron 1260, Solartron Analytical) under open-circuit voltage. The frequency range was from 2 MHz to 0.01 Hz, and the ac amplitude was 10 mV. The cells were then cooled down to room temperature and transferred to a glovebox for disassembly. The cross sections of the cathodes were observed using scanning electron microscopy (SEM, Model JSM-5900LV, JEOL Company, Japan) coupled with energy-dispersive X-ray (EDX) spectroscopy. A few pieces of the cathodes were crushed and ground in an agate mortar to obtain finely grained powders for X-ray diffraction (XRD) analysis. Because of the hygroscopic nature of NaAlCl$_4$ in the cathodes, the samples were prepared in the glovebox. The powder sample was loaded onto an XRD glass sample holder, and the holder was subsequently sealed with Kapton tape. The sealed sample was then put on to the XRD sample stage for XRD analysis. The measurement was carried out at room temperature in the 2θ range of 10–80° with Cu Kα radiation.
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Notes
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REFERENCES

(1) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical Energy Storage for Green Grid. Chem. Rev. 2011, 111, 3577–3613.
(2) Dunn, B.; Kamath, H.; Tarascon, J. M. Electrical Energy Storage for the Grid: A Battery of Choices. Science 2011, 334, 928–935.
(3) Sudworth, J. L.; Tilley, A. R. The Sodium Sulfur Battery. Klauer: New York, 1985; pp 1–30.
(4) Hueso, K. B.; Armand, M.; Rojo, T. High temperature sodium batteries: status, challenges and future trends. Energy Environ. Sci. 2013, 6, 734–749.
(5) Ha, S.; Kim, J. K.; Choi, A.; Kim, Y.; Lee, K. T. Sodium-Metal Halide and Sodium-Air Batteries. ChemPhysChem 2014, 15, 1971–1982.
(6) Lu, X.; Xia, G.; Lemmon, J. P.; Yang, Z. Advanced materials for sodium-beta alumina batteries: Status, challenges and perspectives. J. Power Sources 2010, 195, 2431–2442.
(7) Galloway, R. C. A Sodium/Beta-Alumina/Nickel Chloride Secondary Cell. J. Electrochem. Soc. 1987, 134, 256–257.
(8) Bones, R. J.; Coetzter, J.; Galloway, R. C.; Teagle, D. A. A Sodium Iron(II) Chloride Cell with a Beta-Alumina Electrolyte. J. Electrochem. Soc. 1987, 134, 2379–2382.
(9) Bones, R. J.; Teagle, D. A.; Brooker, S. D.; Cullen, F. L. Development of a Ni,NiCl2 Positive Electrode for a Liquid-Sodium (Zebra) Battery Cell. J. Electrochem. Soc. 1989, 136, 1274–1277.
(10) Moseley, P. T.; Bones, R. J.; Teagle, D. A.; Bellamy, B. A.; Hawes, R. W. M. Stability of Beta-Alumina Electrolyte in Sodium/FeCl2 (Zebra) Cells. J. Electrochem. Soc. 1989, 136, 1361–1368.
(11) Lu, X.; Li, G.; Kim, J. Y.; Lemmon, J. P.; Sprekle, V. L.; Yang, Z. A novel low-cost sodium-zinc chloride battery. Energy Environ. Sci. 2013, 6, 1837–1843.
(12) Li, G.; Lu, X.; Kim, J. Y.; Viswanathan, V. V.; Meinhardt, K. D.; Engellhardt, M. H.; Sprekle, V. L. An Advanced Na–FeCl2 ZEBRA Battery for Stationary Energy Storage Application. Adv. Energy Mater. 2015, 5, 1500357.
(13) Li, G.; Lu, X.; Kim, J. Y.; Lemmon, J. P.; Sprekle, V. L. Cell degradation of a Na–NiCl2 (ZEBRA) battery. J. Mater. Chem. A 2013, 1, 14935–14942.
(14) Ao, X.; Wen, Z.; Wu, X.; Wu, T.; Wu, M. Self-Repairing Function of Ni3S2 Layer on Ni Particles in the Na/NiCl2 Cells with the Addition of Sulfur in the Catholyte. ACS Appl. Mater. Interfaces 2017, 9, 21234–21242.
(15) Li, G.; Lu, X.; Kim, J. Y.; Meinhardt, K. D.; Chang, H. J.; Canfield, N. L.; Sprekle, V. L. Advanced intermediate temperature sodium-nickel chloride batteries with ultra-high energy density. Nat. Commun. 2016, 7, 10683.
(16) Prakash, J.; Redey, L.; Vissers, D. R. Electrochemical behavior of nonporous Ni/NiCl2 electrodes in chloroaluminate melts. J. Electrochem. Soc. 2000, 147, 502–507.
(17) Pan, H.; Shao, Y.; Yan, P.; Cheng, Y.; Han, K. S.; Nie, Z.; Wang, G.; Yang, J.; Li, X.; Bhattacharya, P.; Mueller, K. T.; Liu, J. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Nat. Energy 2016, 1, 16039.
(18) Hertzberg, B.; Sviridov, L.; Stach, E. A.; Gupta, T.; Steinigart, D. A Manganese-Doped Barium Carbonate Cathode for Alkaline Batteries. J. Electrochem. Soc. 2014, 161, A835–A840.
(19) Li, B.; Nie, Z.; Vijayakumar, M.; Li, G.; Liu, J.; Sprekle, V.; Wang, W. Ambipolar zinc-polypyrrole electrolyte for a high-energy density aqueous redox flow battery. Nat. Commun. 2015, 6, 6303.
(20) Weng, G.-M.; Li, Z.; Cong, G.; Zhou, Y.; Lu, Y.-C. Unlocking the capacity of iodide for high-energy-density zinc/polypyrrole and lithium/polypyrrole redox flow batteries. Energy Environ. Sci. 2017, 10, 735–741.
(21) Pan, H.; Li, B.; Mei, D.; Nie, Z.; Shao, Y.; Li, G.; Li, X. S.; Han, K. S.; Mueller, K. T.; Sprekle, V.; Liu, J. Controlling Solid-Liquid Conversion Reactions for a Highly Reversible Aqueous Zinc-Iodine Battery. ACS Energy Lett. 2017, 2, 2674–2680.
(22) Xie, C.; Zhang, H.; Xu, W.; Wang, W.; Li, X. A Long Life Cycle, Self-Healing Zinc–Iodide Flow Battery with High Power Density. Angew. Chem. 2018, 130, 11341–11346.
(23) Cheng, Y.; Luo, L.; Zhong, L.; Chen, J.; Li, B.; Wang, W.; Mao, S.; Wang, C.; Sprekle, V. L.; Li, G.; Liu, J. Highly Reversible Zinc-Ion Interkalation into Chevrel Phase Mo6S8 Nanocubes and Applications for Advanced Zinc-Ion Batteries. ACS Appl. Mater. Interfaces 2016, 8, 13673–13677.
(24) Chang, H. J.; Lu, X.; Bonnett, J. F.; Canfield, N. L.; Son, S.; Park, Y.-C.; Jung, K.; Sprekle, V. L.; Li, G. Development of intermediate temperature sodium nickel chloride rechargeable batteries using conventional polymer sealing technologies. J. Power Sources 2017, 348, 150–157.
(25) Hueso, K. B.; Palomares, V.; Armand, M.; Rojo, T. Challenges and perspectives on high and intermediate-temperature sodium batteries. Nano Res. 2017, 10, 4082–4114.
(26) Robelin, C.; Chartrand, P. Thermodynamic evaluation and optimization of the (NaCl + KCl + MgCl2 + CaCl2 + ZnCl2) system. J. Chem. Thermodyn. 2011, 43, 2015–2015.
(27) Collection of Phase Diagrams. http://www.crtc.polymtl.ca/fact/phase_diagram.php?url=NaCl-ZnCl2.jpg&dir=FTsalt.
(28) Lu, X.; Li, G.; Kim, J. Y.; Lemmon, J. P.; Sprekle, V. L.; Yang, Z. The effects of temperature on the electrochemical performance of sodium–nickel chloride batteries. J. Power Sources 2012, 215, 288–295.
(29) Chang, H.-J.; Canfield, N. L.; Jung, K.; Sprekle, V. L.; Li, G. Advanced Na-NiCl2 Battery Using Nickel-Coated Graphite with Core Shell Microarchitecture. ACS Appl. Mater. Interfaces 2017, 9, 11609–11614.
(30) Lu, X.; Coffey, G.; Meinhardt, K.; Sprekle, V.; Yang, Z.; Lemmon, J. P. High Power Planar Sodium-Nickel Chloride Battery. ECS Trans. 2010, 28, 7.
(31) Lu, X.; Lemmon, J. P.; Sprekle, V.; Yang, Z. Sodium-beta Alumina Batteries: Status and Challenges. JOM 2010, 62, 31–36.