# Effect of sodium iodide additive on the electrochemical performance of sodium/nickel chloride cells

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## Abstract

The effect of sodium iodide and sulfur additives on the performance of $Na/\beta''$-alumina/$NaAlCl_4$/$NiCl_2$/Ni cells was investigated in quasi-sealed laboratory research cells (0.5–1.0 Ah capacity) and in sealed full-size cells (4 Ah capacity). It was found that sodium iodide additive especially in combination with sulfur in $Na/NiCl_2$ cells significantly increases the usable capacity and reduces the impedance of the $Na/NiCl_2$ cells. It is proposed that the use of sodium iodide enhances the energy and power performance of the $NiCl_2$ electrode by two different mechanisms. The first mechanism, iodide ion doping of the anodically formed solid $NiCl_2$, is dominant at potentials lower than that of iodine evolution. The doping effect of the iodide ions produces a higher-capacity, lower-impedance $NiCl_2$ layer on the positive electrode. The second mechanism, anodic formation of very reactive iodine species, is effective when the cell is cycled through the iodine evolution potential range (2.8–3.1 V vs Na). During this process, the dissolved iodine species improve electrode kinetics through liquid-phase mass transport. Use of the sodium iodide additive is safe in sealed cells, causing no over-pressurizing problems. A maximum pressure increase of only 10 kPa was detected by a pressure sensor during severe overcharge tests.

## 1. Introduction

The sodium/nickel chloride battery shows promise for powering electric vehicles because of its high theoretical specific energy (790 Wh $kg^{-1}$) and good cycling characteristics [1–4]. The cell, which operates best in the temperature range 250–340 °C, is similar to the sodium/sulfur cell in that it has a molten sodium negative electrode and a solid $\beta''$-alumina electrolyte. The as-fabricated positive electrode consists of a porous nickel structure (15–20 vol %), NaCl powder (which converts to solid $NiCl_2$ on charge), and a liquid pore electrolyte of $NaAlCl_4$. For the same configuration, sodium/nickel chloride cells a have higher impedance than sodium/sulfur cells. Therefore, sodium/nickel chloride cells have poor power, especially toward the end of discharge. The electrochemical behavior of $NiCl_2$ as the positive electrode in the $Na/NiCl_2$ cells has been extensively studied [4–11]. Most of these studies [6–9] acknowledge that the cell performance is limited due to the $NiCl_2$ electrode. Bones et al. [4] showed that even at low rate cycling the $Na/NiCl_2$ cell suffers with significant capacity degradation. The poor capacity retention

during cycling was attributed to agglomeration of the nickel particles, which reduces the surface area and porosity of the nickel electrode. The addition of sulfur to the liquid sodium tetrachloroaluminate electrolyte was shown to improve the utilization of the nickel chloride electrode [4, 5] during cycling. However, sulfur does not reduce the impedance of the electrode, a key element in cell power. It has also been shown that chemical additives such as sodium iodide (NaI) or sodium bromide (NaBr) significantly improve the specific energy and power of $Na/NiCl_2$ cells, especially at high current densities. These additives increase the area-capacity limit (ACL, defined as the maximum charge uptake on 1 $cm^2$ area of nickel) [7] and also decrease the impedance of the nickel chloride electrode and, thus, increase the specific power. Moreover, cells with these additives can be operated in an exceptionally wide temperature range, between 150 and 400 °C [12]. The decomposition voltage of NaI [13], however, is within the operating voltage range of the $Na/NiCl_2$ cell. Therefore, it is critical to investigate whether iodine gas evolution causes an excessive pressure in a sealed $Na/NiCl_2$ cell and what role it plays in the nickel chloride electrode process.

## 2. Experimental details

Electrochemical investigations of the Na/NiCl$_2$ cell were carried out in quasi-sealed research cells (Figure 1) and sealed full-size cells fabricated by Eagle–Picher which closely simulate the components and operational conditions of the full size battery. The capacity of these cells ranged between 0.5 to 1.0 Ah for the research cells and between 4.0 to 5.0 Ah for the sealed full-size cells. The research cell had a molten sodium negative electrode, a nickel chloride positive electrode, a $\beta''$-alumina tube (CSPL, UK) and a molten electrolyte, Na[AlCl$_4$] containing 2 wt % sulfur (APL Engineered Materials). The molten sodium electrode also served as the reference electrode due to its negligible polarization. The laboratory research cell was operated in a Pyrex glass vessel, which permitted visual observation of the color of the liquid chloroaluminate electrolyte and the gas phase above.

Two types of nickel chloride electrodes were investigated in this study; baseline electrodes with no sodium iodide and improved electrodes with sodium iodide. The electrodes were assembled in the discharged state by mixing Ni 255 (Novamet Specialty Products) and NaCl powders (Aldrich Chemical Co.) and then pressing the material into a pellet with a diameter of 2.80 cm. The pellet was subsequently sintered at 750–890 °C under a reducing atmosphere. The improved porous sintered electrode with better morphology was fabricated by mixing 10 wt % NaI and 10 wt % of the poreformer ammonium bicarbonate with the Ni 255 and NaCl powders and then pressing the material into a 0.5 cm thick pellet. The chemical additive NaI was usually introduced during electrode fabrication in the nickel chloride electrode. In some cases, however, NaI was also introduced directly into the electrolyte. Sulfur, 2 wt % by the electrolyte weight was incorporated into the liquid
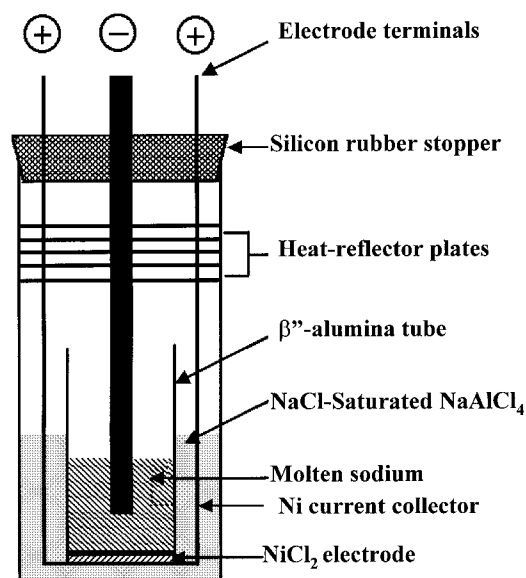


*Fig. 1.* Schematics of the research cell used for Na/NiCl$_2$ studies.

electrolyte of the baseline and improved electrodes. Sulfur was added to stabilize the cell capacity of the cells. These pellets were heated in the furnace first at 150 °C for 1 h to decompose ammonium bicarbonate. During the decomposition of the ammonium bicarbonate at 150 °C, the ejection of NH$_3$, CO$_2$ and H$_2$O vapours produce better porous structure. The pellets were subsequently sintered at 750–890 °C under a reducing atmosphere. After sintering, these electrodes were vacuum impregnated with liquid Na[AlCl$_4$], and then placed in the positive electrode compartment. The positive electrode compartment contained enough NaCl to saturate the liquid even during fully charged conditions.

A uniform one-dimensional current distribution was maintained in the nickel chloride electrode galvanostatically in the anodic (3.0 V) and cathodic (2.0 V) directions against a Na electrode. In the static measuring mode the current interruption technique was used during the cycling to evaluate the electrode and cell impedance. To obtain direct proof of the performance-enhancing effect of NaI and iodine, a Na/NiCl$_2$ laboratory research cell was built that had a 0.25 cm thick sintered nickel chloride electrode. This cell was operated for 176 cycles without NaI additive. After this cycling period, NaI and S were added to the cell electrolyte. The electrochemical performance of this cell was monitored before and after the addition of NaI into the cell.

The pressure effect due to iodine evolution was investigated in the sealed full-size cell. The sealed cell consisted of an 'inside' nickel chloride positive electrode, a $\beta''$-alumina tube, and a sodium electrode. The cell was inserted into a steel cell container and hermetically sealed with a ceramic header seal. The pressure inside the positive electrode compartment was measured using a high-temperature pressure gauge. The pressure gauge was attached to the positive electrode compartment via a nickel tube and operated isothermally with respect to the temperature of the cell, thereby avoiding any condensation in the pressure-sensing bellows. The pressure was measured during standard charge/discharge cycling in the voltage range 1.9–3.1 V at various current densities and also during overcharges up to 4.4 V.

## 3. Results and discussion

Figure 2 shows the discharged voltage profiles as a function of discharged capacity per unit volume of electrode for the baseline and improved cells. Both cells were fabricated with 2 wt % sulfur in the electrolyte. The need for the sulfur additive in the nickel chloride electrodes is due to poor cycling efficiency of the Na/NiCl$_2$ cells. It has been shown [4, 5] that the Na/NiCl$_2$ cells fabricated without sulfur additive have very poor cycling efficiency with a 50% capacity loss within 10 cycles. This capacity loss was attributed to agglomeration of the nickel particles, which reduces the surface area and porosity of the nickel electrode. The addition of sulfur to the liquid sodium tetrachloroaluminate
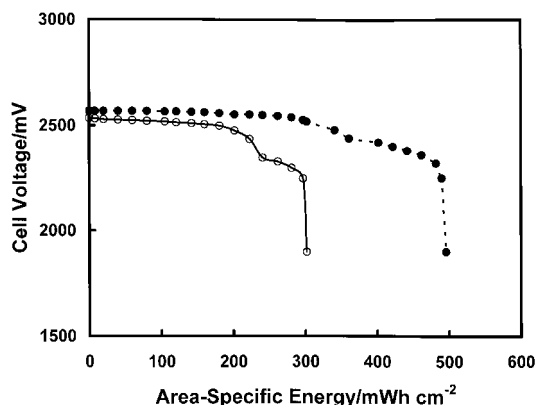
Fig. 2. Effect of the NaI additive on the cell voltage and discharge capacity of the Na/NiCl$_2$ research cells during the discharge half-cycles at 300 °C. Cells were discharged at a constant 20 mA cm$^{-2}$. Key: (O——O) baseline electrode; (●- - - ●) improved electrode.

electrolyte improves the utilization of the nickel chloride electrode [4] during cycling. The addition of sulfur improves the electrode utilization by preventing the grain growth of nickel particles during cycling. Therefore, sulfur was added to stabilize the capacity of baseline and improved Na/NiCl$_2$ cells in this study. The usable capacity of the electrodes defined in this figure is the discharged capacity when the cell voltage drops to 1.9 V. The presence of a lower plateau at 2.3 V in Figure 2 is due to the partial reduction of the sulfur in the cell on discharge. Area-specific impedance (ASI$_{15s}$), measured by an interrupted galvanostatic method, as a function of discharged capacity per unit volume for the baseline and improved NiCl$_2$ electrodes is shown in Figure 3. The area-specific impedance (ASI$_t$) is time dependent and includes the resistance, capacitance, and inductance components of the electrode. The ASI$_t$ is an important property of the electrode in that it provides information regarding the nature and the magnitude of the electrochemical and mass-transport limitations. The ASI$_{15s}$ was measured by a d.c. current interruption technique by measuring the cell voltage relaxation for
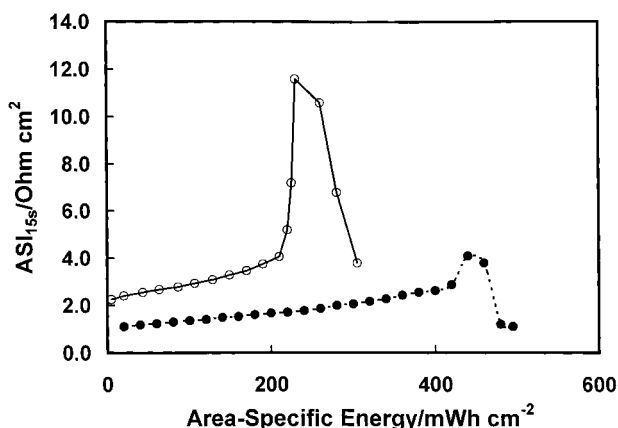
15 s. The ASI$_{15s}$ was calculated by dividing the relaxation value of the voltage by the current density applied before current interruption. The usable capacity defined in this figure is the discharged capacity when the area-specific impedance (ASI$_{15s}$) reaches 4 $\Omega$ cm$^2$ or the cell voltage drops to 1.9 V. The termination points of the curves at higher utilized capacities for the improved electrode indicate increased available energy density (Wh cm$^{-3}$), and the lowered area-specific impedance of the nickel chloride electrode ($\Omega$ cm$^2$) indicates higher power capability. The ASI of the nickel chloride electrode was calculated by subtracting the ASI of the Na/$\beta''$-alumina electrode, which was measured in separate experiments, from the cell value. Figures 2 and 3 show that sulfur does not reduce the impedance of the electrode, a key element in cell power. However, the use of NaI additive significantly improves the electrode performance, as shown by the higher available specific energy and the much lower area-specific impedance in Figure 3. This favourable effect is probably due to a doping mechanism, which is also affected by the different solubilities of NiCl$_2$ and NiI$_2$ [14].

Figure 4 shows improved cell performance between cycles 176 and 181. The cell performance is defined qualitatively in terms of the capacity achieved in the 1.9–3.1 V cycling range and the area-specific impedance of the nickel chloride electrode. It can be seen from this Figure that the cell performance improved immediately when NaI and S were added, as indicated by the extended cell capacity and the somewhat lowered impedance in cycle 177. The substantial performance improvement for further cycles, when the additives gradually reached the deep pores of the electrode, is quite evident from the Figure. During charge of the research cell at about 2.8 V, the characteristic violet color of iodine appeared in the molten electrolyte and gradually also in the gas phase. The colour indicated the anodic evolution of iodine from NaI. The violet liquid phase visible in the pyrex glass vessel (Figure 1) indicated the high solubility of iodine in the molten
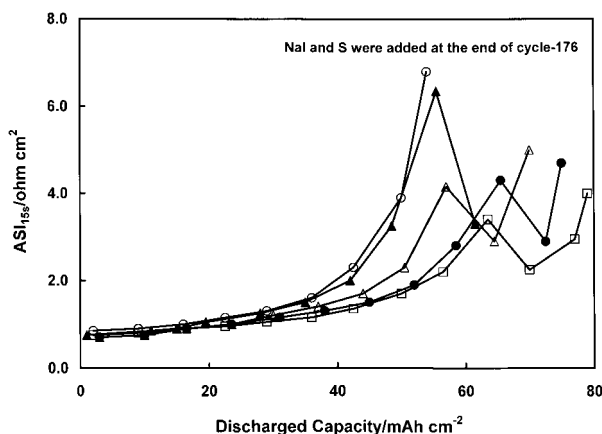


Fig. 3. Effect of the NaI additive on the area-specific impedance of the Na/NiCl$_2$ research cells during the discharge half-cycles at 300 °C. Cells were discharged at a constant 20 mA cm$^{-2}$. Key: (O——O) baseline electrode; (●- - - ●) improved electrode.



Fig. 4. Area-specific impedance (ASI$_{15s}$) of a Na/NiCl$_2$ research cells as a function of discharged capacity. Increased usable capacity and lowered impedance were measured when NaI and S were added. Cycle: (O) 176, (▲) 177, (△) 178, (●) 180 and (□) 181.

chloroaluminate. The equilibrium pressure of iodine, however, was not measured in the quasi-sealed cell.

The cells fabricated by Eagle–Picher were designed to verify the performance of the baseline and improved research cells in sealed full-size cells. The cells were designed in such a way that the performance parameters could be precisely measured and the internal conditions could be monitored to study iodine pressure during overcharge conditions. The performance of the 4 Ah sealed Na/NiCl$_2$ sealed full-size is shown in Figure 5 in terms of nickel utilization. Figure 6 shows such a comparison between the area-specific impedance measured in research and sealed full-size cells. It is clear form the data that although the sealed full-size cells were not completely optimized, they still demonstrated good performance which was consistent with the research cell measurements.

Only a small pressure increase (1–2 kPa) was observed in the improved cell, in the critical iodine-producing voltage range above 2.8 V under normal charge conditions ($< C/2$ current and cell voltage $< 3.1$ V). However, as Figure 7 shows, a more pronounced, although still insignificant, overpressure (about 10 kPa) developed
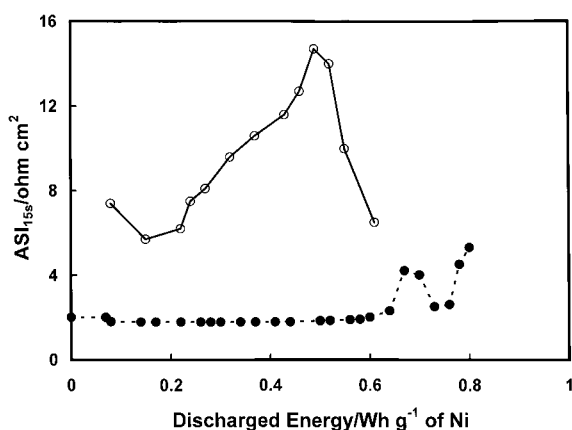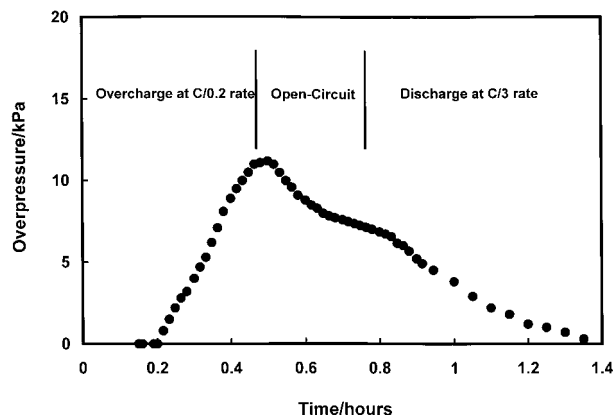


Fig. 7. Overpressure during severe overcharge in the sealed full-size Na/NiCl$_2$ cell. Cell was overcharged with $C/0.2$ current to 4.4 V.

under forced, unusually severe overcharge tests at 350 °C, during which time a $C/0.2$ current was applied, and the cell voltage was allowed to reach 4.4 V. During this overcharge test, the cell temperature increased by 15 °C. When the charging current was terminated (at the peak pressure in Figure 7) and the cell was left on open circuit, the pressure gradually decreased. The subsequent discharge caused the pressure to drop at a faster rate until it attained its pre-overcharge value.

It was concluded from these experiments that NaI additive in combination with sulfur in Na/NiCl$_2$ cells significantly increases the usable capacity and reduces the impedance of the Na/NiCl$_2$ cells. It is proposed that the NaI additive enhances the performance of the nickel chloride electrode by two different mechanisms. The first mechanism is dominant at potentials lower than the potential for iodine evolution ($\sim$2.8 V vs Na). The iodide ions help to develop a higher-capacity, lower-impedance NiCl$_2$ layer compared with an additive-free experiment. The trend in the capacity and the area-specific impedance (Figure 3) is consistent with the studies reported on nonporous nickel electrodes [10]. It has been shown [7, 10] that although a certain limited capacity (ACL) can be achieved on the surface of nickel, the addition of iodide ions produces a higher capacity, lower-impedance of the NiCl$_2$ electrode compared with an additive-free electrode system [10]. The improvement in terms of increased capacity and reduced ASI is attributed to the modification of the chemistry and morphology of the solid NiCl$_2$ layer in the presence of iodide ions [10]. The increase in ACL is significantly more than the charge equivalent associated with NaI addition, showing that the additive changes the chemistry and perhaps also the morphology of the NiCl$_2$ layer. The second enhancement mechanism occurs when the cell is cycled through the iodine evolution potential range (2.8–3.1 V). The ACL is extended further, and the impedance of the doped NiCl$_2$ layer becomes even lower, allowing for a very high power discharge, which is needed, for example, to propel an electric vehicle. Figure 8 shows the voltage profiles of the baseline and improved cell during the charge process. A voltage



Fig. 5. Area-specific impedance (ASI$_{15s}$) of sealed full-size Na/NiCl$_2$ cells as a function of discharged capacity. Cells were discharged at a constant 20 mA cm$^{-2}$. Key: (O——O) baseline electrode; (●- - - - ●) improved electrode.
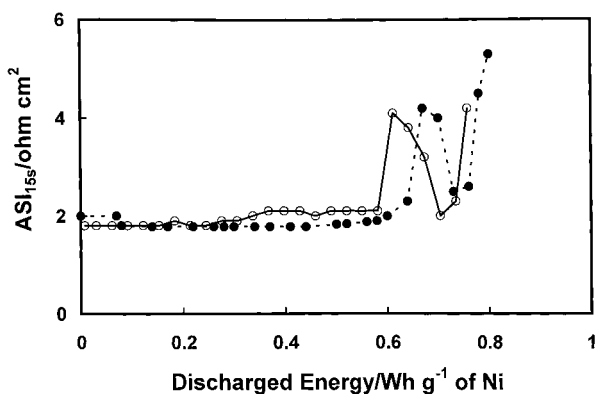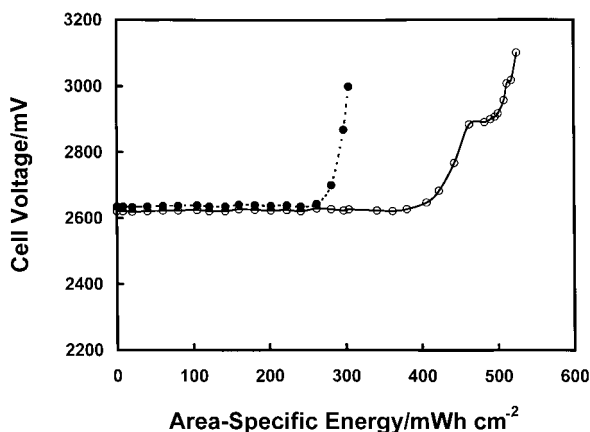


Fig. 6. A comparison of the area-specific impedance of the improved electrode measured in the research and the sealed full-size Na/NiCl$_2$ cells. Key: (O——O) research cell; (●- - - - ●) sealed full-size cell.

*Fig. 8.* Effect of the NaI additive on the cell voltage and capacity of the Na/NiCl$_2$ research cells during the charge half-cycles at 300 °C. Cells were charged at a constant 20 mA cm$^{-2}$. Key: (O——O) improved electrode; (●- - - ●) baseline electrode.

plateau at about 2.85 V in the charge curve of the improved electrode (Figure 8) is attributed to iodine evolution. The violet gas phase visible in the pyrex glass vessel (Figure 1) above 2.85 V during charge reaction of the improved electrode also confirmed the iodine evolution. The voltage plateau 2.85 V, however, was less evident at high charge rates and after extensive cycling. The substantial performance improvement for further cycles, when the additives gradually reached the deep pores of the electrode, is quite evident in Figure 4. This improved mechanism can be explained by the formation of highly soluble iodine species that can easily diffuse in the liquid chloroaluminate to new reaction sites and thereby improve the kinetics of the electrode reaction. The existence of poly- and interhalogen ions has been documented in chloroaluminate melts [14–16]. The iodine species in the high potential range ($V > 2.8$ V) have strong oxidizing power and can further oxidize nickel metal surface to produce additional capacity. The chemical consumption of the anodically produced species and I$^-$ gas via dissolution and reaction with the porous nickel is evidenced by the diminishing overpressure on open circuit (Figure 7). The performance-improving synergistic effect of sulfur and iodine may be attributed to the formation of SI$_3^-$ species, which is analogous to the earlier proposed SCl$_3^-$ ion [14]. Further research is needed, however, to give a full account of this very complicated iodine effect on the nickel chloride electrode.

## 4. Conclusions

Sodium iodide additive, especially in combination with sulfur, in Na/NiCl$_2$ cells significantly increases the usable capacity of a given amount of porous nickel electrode and also decreases considerably the cell impedance. By use of a combination of sodium iodide additive and improved cell design, the usable capacity of the Na/NiCl$_2$ cell during high-rate discharge and charge can be increased five times and the area-specific

impedance can be reduced to one-third that of an additive-free cell. At the end of a charge, greater than 2.8 V, iodine forms anodically. Iodine evolution, however, does not increase the gas pressure inside a sealed cell more than about 10 kPa, even at prolonged or very high rate overcharges. The measured pressure increase is much less than the calculated increase if all iodine were to be in the gas phase. The reduced pressure is explained by the high solubility of iodine in liquid chloroaluminate and the reaction between iodine and nickel metal. Consequently, the use of a performance-enhancing additive, such as NaI, does not jeopardize the integrity of high-performance, sealed Na/NiCl$_2$ cells.

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