Effects of sulfur additive on the performance of Na/NiCl$_2$ cells

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Abstract

NiCl$_2$ electrode in Na//β''-alumina//NaAlCl$_4$//NiCl$_2$ high-temperature rechargeable cells undergoes a morphological change during charge/discharge cycling, which results in a rapid capacity decline and premature cell failure. Addition of sulfur was reported to have prevented this morphological change and improved the cycle life of the cells significantly. Our earlier, single electrode studies indicate that the sulfur additive also improves the kinetics of NiCl$_2$. A detailed study on the effects of the sulfur additive on the performance of NiCl$_2$ electrode is reported here. Different methods of NiCl$_2$ electrode fabrication are examined to improve its charge efficiency. The sulfur content in the electrolyte is optimized based on the charge/discharge cycling and SEM micrographs. Other (non-sulfur) less corrosive additives, based on transition metals are examined for alleviating the morphological change during cycling. A combination of the transition metal additives and sulfur is expected to have a synergistic beneficial effect on the cycle life of NiCl$_2$ electrode.

Introduction

A new class of high-temperature, sodium rechargeable batteries based on transition metal chlorides as positive electrodes have emerged in the last decade [1, 2]. These systems are similar to the Na/S batteries in terms of anode half-cell and the (high) energy densities. In addition, the use of solid metal chloride cathodes in basic chloroaluminate melts results in several significant advantages, including lower operating temperatures, improved safety and higher reliability. Extensive developmental efforts have been made at CSIRO in South Africa and at Harwell and Beta Power in England [3–5]. Excellent performance characteristics have been demonstrated with both Na/FeCl$_2$ and Na/NiCl$_2$ systems in small and large cells as well as in batteries.

The research effort at the Jet Propulsion Laboratory (JPL) has focused mainly on understanding the basic electrochemical behavior of the metal chloride cathodes, i.e., in verifying the electrochemical reversibility, elucidating the reaction mechanisms, estimating the rate parameters and identifying the rate-limiting processes [6–8]. Several transition metal chlorides have been evaluated [9] from which NiCl$_2$ has been chosen for further developmental studies for space applications due to its higher energy density and reversibility. One of the problems associated with the use of NiCl$_2$ is an agglomeration of the electrode particles causing a premature failure in the cycle life. Fortunately, this can be alleviated by an addition of sulfur to the chloroaluminate electrolyte [5]. NiCl$_2$ electrodes have thus performed admirably in the sulfur-containing electrolyte with cycle lives well over 2000 cycles [5]. Prompted by the success achieved with the

sulfur additive in improving the morphology of the $NiCl_2$ electrode, we carried out basic electrochemical studies on the effects of the sulfur additive [10], which point out that sulfur also enhances the kinetics and improves the chargeability of the $NiCl_2$ electrode. In this work, the effects of the sulfur additive on the performance characteristics of $NiCl_2$ during charge/discharge cycling have been examined. Also, the possibility of using non-sulfur, more compatible additives based on transition metals has been tested. Additionally, the methods of electrode fabrication have been improved to achieve increased electrode porosity and performance.

Experimental

Sodium–nickel chloride test cells were of central cathode design. A stainless-steel tube acted as cell container as well as negative terminal. A β''-alumina solid electrolyte tube placed inside the stainless-steel tube separated the cathode and anode half-cells. The columnar volume between the stainless-steel tube and the beta tube contained enough sodium to make the cells cathode limited. The insides of the beta tube were filled with sodium tetrachloroaluminate fused salt electrolyte. The sintered $NiCl_2$ electrode immersed in the molten salt acted as the positive electrode. The cell design is essentially similar to that adopted by British Rail for Na/S cells, with a mechanical compression seal. For the fabrication of the $NiCl_2$ electrode, INCO nickel power type 255 ($\sim 3~\mu m$) was used. Sodium chloride obtained from Aldrich was preheated and pulverized to get a particle size less than 100 μm. Sodium tetrachloraluminate as received from Johnson Matthey was premixed with 5 wt.% powdered NaCl. The cells were housed in cylindrical aluminum blocks heated with a heating tape and holding about five cells each. The cell-to-cell variations in the temperature were thus eliminated. β''-alumina tubes received from Ceramatec Inc. were cleaned by etching in hot phosphoric acid followed by baking at a temperature of ~ 800 °C. All the cell fabrication and testing operations were carried out in an argon-filled glove box. Cell cycling was performed by a Macsym system developed in-house. Morphological studies on the cycled electrodes were made using scanning electron microscopy (SEM). All the experiments were carried out at a temperature of 275 °C, unless specified otherwise.

Results and discussion

The $NiCl_2$ electrodes were fabricated by a cosintering of fine powders of Ni and NaCl mixed in the mole ratio of 3:1. On formation, one third of the Ni would thus be chlorinated, with the rest of the Ni acting as its grid. The built-in capacity of the electrode would correspond to its NaCl content.

Before the sintering process, the electrode powders were pressed at a minimum pressure. Loose sintered electrode from type 255 Ni powder would have a volume porosity in excess of 85% [11], which decreases both during pressing carried out before sintering and due to NaCl addition. $NiCl_2$ electrodes could also be made by loose sintering, simply by filling the beta alumina tube with the electrode powders and producing sintered-like structure during initial charge [12]. However, such electrodes would not permit any postmortem analysis unless the beta tubes are crushed. For the present study, therefore, the electrodes were pressed before sintering for ease of dismantling after cycling, while focusing on high electrode porosity.

The first batch of the electrodes were fabricated in prismatic configuration at a compaction pressure of 10 000 psi. The electrodes obtained (1 Ah) are fairly dense,

TABLE 1

Coulombic efficiencies and physical characteristics of $NiCl_2$ electrodes fabricated by different methods of pressing prior to sintering

Electrode description	Charge density (mAh/cm³)	Apparent area (cm²)	Porosity (%)	Charge efficiency (%)
Rectangular block	575	12.9	31	22 at 13 h
				48 at 30 h
				54 at 40 h
Foil (spiral or corrugated)	~150	90		98 at 22 h
Cylindrical (split mold)	490	15.8	37	45 at 10 h
				70 at 20 h
				~100 at 40 h
Loose sintered	296	48	60	~100 at 20 h

the charge density being 575 mAh/cm³. Expectedly, its conversion efficiency is poor. At rates of 75 mA (13 h), 30 mA (30 h) and 20 mA (40 h), the electrode has conversion efficiencies of 22, 48 and 54%, respectively (Table 1). The low porosity of electrode prevents the access of the electrolyte to the interior portions of the electrode. The next batch of electrodes was made in cylindrical shape with a split mold, in order to extract the electrode easily from the mold. Pressures enough to handle the electrode before sintering were adopted. These electrodes (2 Ah) also have a high charge density of 490 mAh/cm³. The conversion efficiency of the electrodes has, however, improved to 60% at a rate of 100 (20 h) and increased to 70% after one charge/discharge cycle. The conversion efficiency decreased to 45% at 200 mA (10 h) but increased to ~100% at 25 to 50 mA (80 to 40 h) (Table 1). The next generation of electrodes was fabricated in loose sintered form. The cylindrical mold was filled with the electrode powders and the electrode was sintered while being retained in the mold. These electrodes (2 Ah) appeared highly porous and have a low charge density of 296 mAh/cm³. The current efficiencies of these electrodes are accordingly high, ~100% at a charge rate of 100 mA (20 h) (Fig. 1, Table 1).

It is interesting to note that the discharge efficiencies in all the above electrodes are high (above 90%), suggesting that the portions of the electrodes participated in the charging process are fairly efficient in the subsequent discharge.

The sintering of the electrode was carried out in an inert (argon) atmosphere at temperatures slightly below the melting point of NaCl (801 °C) for a period of 2 h. In subsequent experiments, the sintering was carried out for only 15 min and in a reducing atmosphere (3% hydrogen).

Flat electrodes

One of the aspects Na/NiCl$_2$ fail in comparison with the Na/S cells is the power capability; the power densities are lower as compared with Na/S batteries, mainly due to polarization losses at the cathode [13]. It was suggested from an optimization study [14], aimed at space applications, that the optimum thickness of the electrode is 4 mm after which diffusional losses set in. With such a constraint on the electrode dimensions, it may be difficult to achieve reasonable energy densities with Na/NiCl$_2$
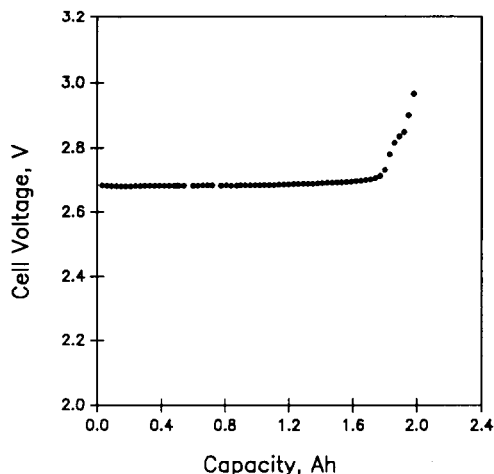
Fig. 1. Initial charging curve of a 2-Ah a 'loose-sintered' $NiCl_2$ electrode in a $Na/NiCl_2$ test cell at 275 °C illustrating a high conversion efficiency for the electrode.

cell. Accordingly, alternate designs (non-cylindrical) have been examined for the electrodes.

Flat $NiCl_2$ electrodes were fabricated by mixing the electrode powders with a binder, for example, elastomeric binder such as ethylene propylene diene monomer (EPDM) (polytetrafluorethylene may also be used). The binder material would be decomposed and vaporized during sintering. It is then possible to fabricate a large-area sheet electrode either by coating (painting) or rolling onto a nickel Exmet. Such an electrode may either be spirally wound or folded with corrugations to accommodate into the beta alumina tube. Electrodes thus made have a high geometrical area of 85 cm^2/Ah as compared with cylindrical electrodes (~ 25 cm^2/Ah). These electrodes have high conversion efficiencies of $\sim 98\%$ at a rate of 50 mA (22 h) (Fig. 2). The rate capabilities of the electrodes are expected to be superior to the cylindrical electrodes. Though the primary current distribution appears to be non-uniform, especially in the spirally wound design, the high conductivity of the molten salt might offset this. Such sheet electrodes may also be made with a doctor's blade technique without any binder as is commonly done with sintered Ni plaques in Ni/Cd batteries.

Effects of sulfur additive

As mentioned before, sulfur additive has been reported to prevent the morphological change and the resulting capacity decline of the $NiCl_2$ electrode [5]. The $NiCl_2$ electrode is reportedly more porous after cycling upon the addition of sulfur to the electrolyte [15]. In order to confirm this, 2-Ah cells were fabricated with no additive and with 2 wt.% sulfur. These cells were cycled between 2.0 and 3.0 V versus Na^+/Na. Sulfur tends to participate in the electrochemical reaction at 2.1 V. It is not clear whether the discharge of $NiCl_2$ should proceed all the way to the sulfur reaction. The effect of such a deep discharge on the cycle life of $NiCl_2$ needs to be understood. In other words, it is ambiguous if sulfur can retain its beneficial effect even in the reduced state. The charge/discharge curves of the 2-Ah cells with and without sulfur additive
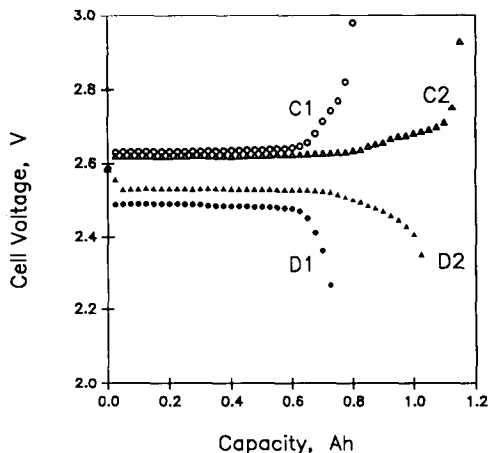
Fig. 2. Charge/discharge curves of 1.2-Ah spirally wound $NiCl_2$ foil electrode fabricated with a binder (EPDM) prior to sintering: (C_1) 1st charge at 75 mA; (D_1) 1st discharge at 150 mA; (C_2) and (D_2) are at 50 mA and 75 mA, respectively.
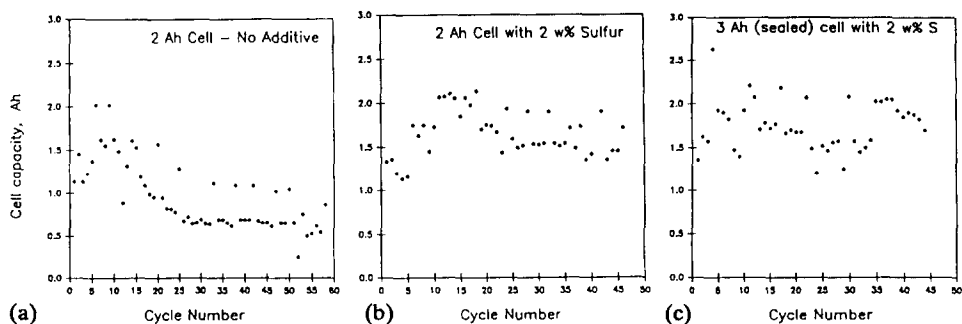

Fig. 3. Variation of capacity $Na/NiCl_2$ cells with and without 2 wt.% sulfur additive to the electrolyte, during cycling at $C/10$ discharge and $C/10$ charge. Higher capacities were obtained in discharges following low rate ($C/40$) charging.

indicate that the cells containing sulfur have higher charge voltages and lower discharge voltages. This may be attributed to the increased catholyte resistance upon sulfur addition. In concurrence with this, the a.c. impedance data indicate that the internal resistance of cell with sulfur is higher (1.2 Ω as compared with 0.65 Ω for a standard cell).

These cells have been typically charged at $C/20$ (or $C/40$) and discharged at $C/10$ rate. The variation of the cell capacity with cycle number in these cells is shown in Figs. 3(a) and (b). The capacity of the standard cell started falling sharply from 12th cycle and reached a plateau value of 0.6 Ah (about 40% of the initial value) within 25 cycles. It is important to note that the failure of the cell appeared to be a hindered charging process. The discharge efficiency, on the other hand, continued to be high. Charging of the $NiCl_2$ electrode involving dissolution of NaCl has been realized to be a slow process [5]. The charging process appears to be critically dependent on the electrode porosity. The cell with the sulfur additive instead appears to have a more stable capacity. Its capacity increases to ~ 2.0 Ah around 10 to 17 cycles and

stabilized at 1.6 Ah. At the end of 45 cycles, the cell capacity reaches a plateau around 1.6 Ah (above 90% of its initial value). The beneficial effect of sulfur additive can also be seen in the 3-Ah sealed cell (Fig. 3(c)). The capacity reached a plateau of 1.6 Ah after 45 cycles.

A.c. impedance and d.c. polarization measurements were carried out on these cells during cycling, in order to establish a correlation, if any, between the area-dependent kinetic parameters, e.g., charge-transfer resistance and double-layer ca-pacitance, and the morphological change. No direct correlation has emerged so far from the a.c. impedance behavior. The polarization resistance from d.c. micropolarization is lowered (0.69 versus 0.79 Ω) with the sulfur additive (Fig. 4). The corresponding values for the exchange-current density, based on apparent or geometric area, are 0.73 and 0.62 mA/cm^2 for the reduction of NiCl$_2$, in electrolytes without and with the sulfur additive, respectively. The Tafel behavior is identical for the cells with and without the sulfur additive on the reduction side (Fig. 5). The Tafel slopes obtained from these plots are 0.39 and 0.42 V in the cells without and with the sulfur additive, respectively for the reduction of NiCl$_2$. The corresponding values of transfer coefficients are also identical, i.e., 0.14 and 0.13, respectively. During oxidation, however, the overpotentials are higher with the sulfur additive (Fig. 5) and a good Tafel behavior is absent. The higher overpotentials may be attributed to increased ohmic polarization with the sulfur addition. The poor Tafel behavior may be due to an interference from an additional charge-transfer step in this range of overpotentials. The anodic Tafel slope for the cell without sulfur is estimated as 0.44 V, which corresponds to a transfer coefficient of 0.12. The exchange current densities calculated from the Tafel plots show the same trend as the linear polarization data and decrease in the sulfur-containing cell to 1.62 mA/cm^2 as compared with 2.82 mA/cm^2 for the standard (with no additive) cell. It follows from the above studies that the kinetics of NiCl$_2$ are not hampered by the morphological change. In other words, the decline in the capacity
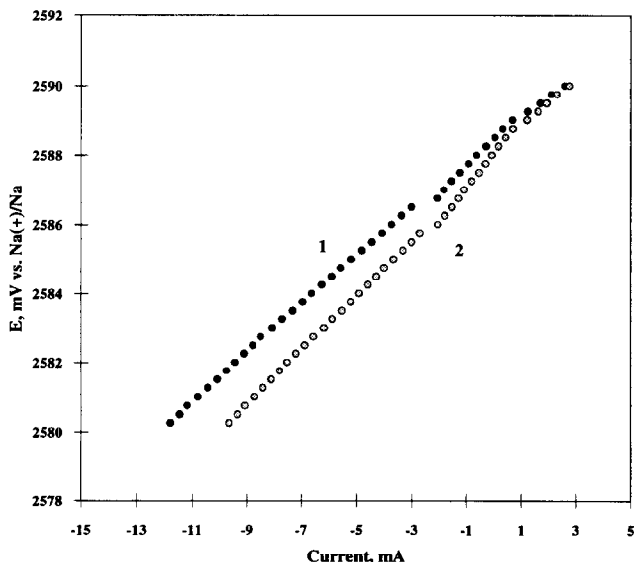

Fig. 4. D.c. linear polarization curves of NiCl$_2$ electrode in NaAlCl$_4$ electrolyte: (1) with no additive, and (2) with 2 wt.% sulfur, after cycling for 58 and 46 cycles, respectively.
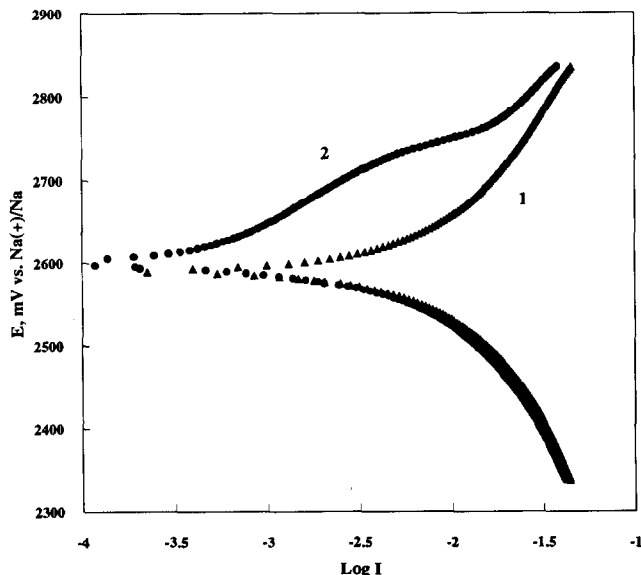
Fig. 5. Potentiodynamic (Tafel) polarization curves, at 0.5 mV/s, of $NiCl_2$ electrode in $NaAlCl_4$ electrolyte: (1) with no additive, and (2) with 2 wt.% sulfur, after cycling for 58 and 46 cycles, respectively.

of the standard cell (with no additive) cannot be explained in terms of poor kinetics. The improvement in chargeability in the sulfur-containing cells may be attributed to the additional charge-transfer step appeared during oxidation (charging), which is related to the sulfur. This reaction involving the oxidation of sulfur may act as a precursor to the oxidation of $NiCl_2$ and thus facilitates the charging of the $NiCl_2$, which has been identified as a slow and critical step as compared with the reduction.

Postmortem analyses carried out on the cells revealed that in the cell without additive, the electrode appears to have hardened during cycling, possibly due to agglomeration. It was found to be difficult to disassemble the electrode from the beta" tube, whereas the electrode cycled in sulfur-containing electrolyte appeared powdery and could be easily removed. SEM micrographs reveal that there is a considerable agglomeration in the electrode during cycling in the absence of sulfur additive. Figures 6(a)–(d) illustrate the SEM micrographs of the $NiCl_2$ electrode before cycling (i.e., after sintering), after 60 cycles in sulfur-free electrolyte, after 50 cycles 2-Ah cell with 2% sulfur and after 40 cycles in 3-Ah cell with 2% sulfur, respectively. The grain size has increased from an initial value of ~15 to 50–60 μm during cycling in the cell without additive. With the sulfur additive, on the other hand, the grain size is reduced to 5–10 μm in the 2-Ah cell and 3–10 μm in the 3-Ah cell. Besides, the electrodes cycled in the sulfur-containing electrolytes appear highly porous.

Optimization of sulfur

As mentioned above, sulfur is a desirable additive to the electrolyte for improved capacity retention of the $NiCl_2$ during cycling. However, higher amounts of sulfur are certainly deleterious to the cell, since it can result in an increase in the internal
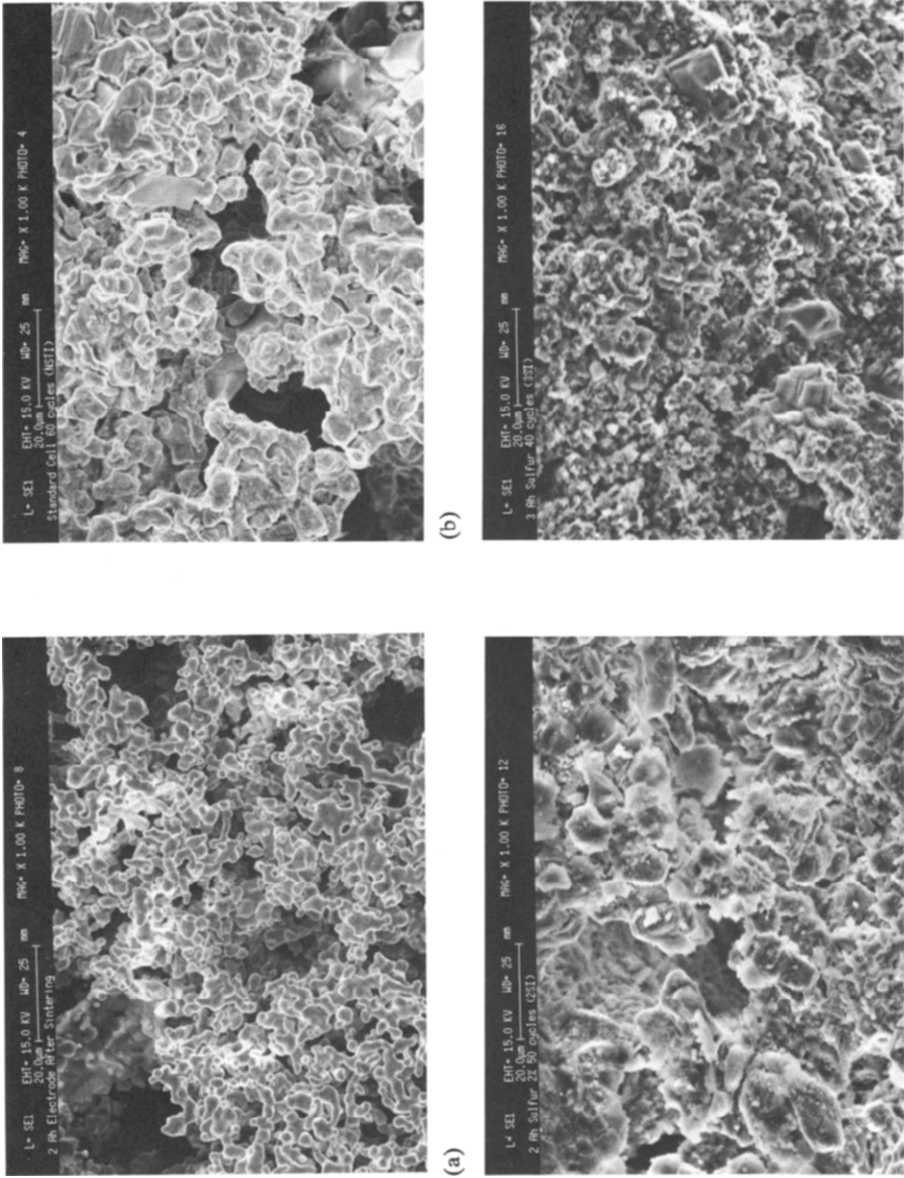
Fig. 6. Scanning electron micrographs of $NiCl_2$ electrode: (a) before cycling and after cycling in the electrolyte; (b) with no additive; (c) with sulfur in 2-Ah cell, and (d) with sulfur in 3-Ah cell.
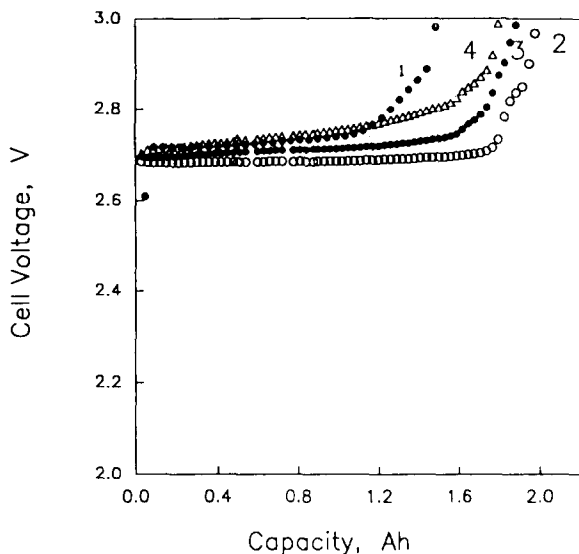
Fig. 7. Initial charge curves of 2-Ah Na/NiCl₂ cells in electrolyte: (1) without additive; (2) with 1.0 wt.; (3) 1.5 wt.%, and (4) 2.0 wt.% sulfur, illustrating the beneficial effect of sulfur on initial charge.

resistance and corrosion of the cell container/positive current collector. Also, it was observed from the single-electrode studies that higher sulfur amounts in the electrolyte might affect the electrochemical reversibility of NiCl₂ [16]. Accordingly, Na/NiCl₂ cells were constructed with different amounts of sulfur additive in the electrolyte and tested in order to identify the minimum amount of sulfur required to retain the morphology and stabilize the capacity of NiCl₂ during cycling. These studies indicate that:

(i) The conversion efficiency increases upon the addition of sulfur, maximizing at 1%. The conversion efficiencies are 75, 92, 99, 95 and 91% with 0, 0.5, 1.0, 1.5 and 2.0% sulfur, respectively (Fig. 7).

(ii) The charging voltages increase with increasing sulfur content and are consistent with the cell internal resistance values obtained from a.c. impedance, i.e., 0.60, 0.82, 0.80 and 0.84 Ω for cells containing 0, 0.5, 1.0 and 2.0 wt.% of sulfur in the electrolyte, respectively.

(iii) The sulfur content in the range of 0.5 to 1.0% is sufficient to prevent the capacity decline. For example, the variation of capacity during cycling for the cell with 0.5% sulfur is shown in Fig. 8 and compared with the standard cell (i.e., without any additive). The cell without any additive expectedly has a rapid decline in the capacity, whereas the cell with 0.5% of sulfur has a steady capacity. This cell has so far been cycled for over 170 cycles and the capacity reaches a plateau around 1.5 Ah (above 80% of the initial value). With this sulfur content, the increase in the internal resistance of the cell upon the sulfur addition is minimum, as may be seen from the cell impedance values obtained from a.c. impedance.

Non-sulfur additives

In view of the possible corrosion problems associated with the use of sulfur as an additive to the cathode, a search has been made for non-sulfur and non-corrosive
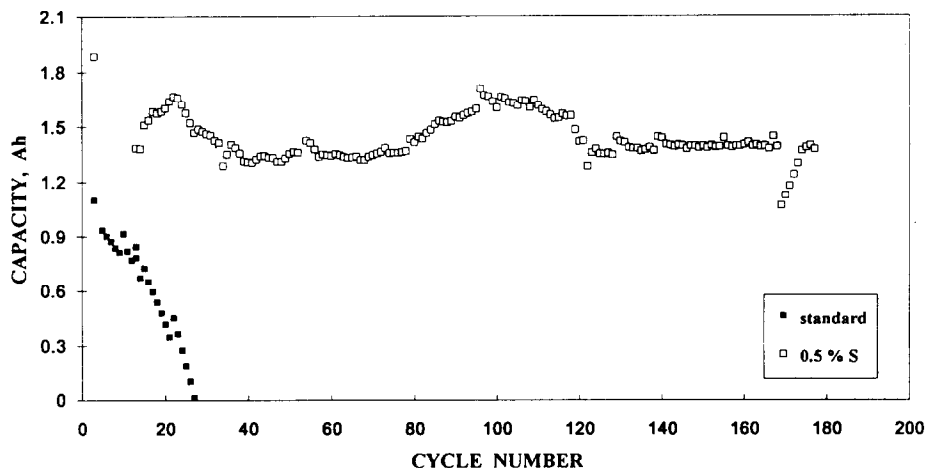
Fig. 8. Variation of capacity of 2 Ah 'loose-sintered' NiCl$_2$ electrode in NaAlCl$_4$ electrolyte (■) with no additive, and (□) with 0.5% sulfur, during cycling at 10-h rate.

additive based on transition metal chlorides. Specifically, transition metals such as cobalt, manganese and iron have been mixed in the ratio of 10 wt.% with the cathode. Substitution of 10 wt.% of nickel with the above metals has no adverse effect on the quality of the sintered structure. Because of the potentials of the corresponding chlorides being lower than of NiCl$_2$, there would be a chlorination of the these metals during charge, thus forming a mixed chloride cathodes. A uniform dispersion of these additives in the cathode matrix might prevent agglomeration of nickel particles and retain the morphology/capacity of the electrode. Besides, these additives are more compatible with the cell components and pose no corrosion problems to the positive current collector (usually nickel), since nickel is thermodynamically stable towards these metals.

For the charge/discharge curves, it is clear that a distinct voltage plateau corresponding to the metal additive may be seen especially with cobalt and iron (Fig. 9). The plateaus due to cobalt and iron chlorides occur at ~50 and 250 mV less than of Ni, respectively. The corresponding chlorides, i.e., FeCl$_2$ and CoCl$_2$ are insoluble in the chloroaluminate electrolyte [9], which rules out the possibility of β''-alumina being poisoned by these metal ions. Manganese, on the other hand, would not undergo any reversible electrochemical reaction on the potential range studied.

Cells of 2-Ah capacity and containing 10% iron, cobalt or manganese as additives to the cathode were cycled and compared with the standard (without additive) cell (Fig. 10). As may be seen from this Fig., cells with the metal additives exhibit slightly better capacity retention than standard cells. Besides, the additives also undergo reversible electrochemical reaction in the potential range of 2.0 to 3.0 V, thus contributing to the cell capacity and energy density which otherwise would have decreased. The cell with cobalt failed prematurely, possible due to a failure of the solid electrolyte. The internal resistance values obtained from a.c. impedance are 0.60, 0.77, 0.92 and 0.73 Ω for the standard cell and the cells with cobalt, iron and manganese, respectively.

The beneficial effect of the metal additives is not as prominent as with sulfur. Nevertheless, it may be possible that a combination of transition metal addition to the electrode and sulfur to the electrolyte can have a synergistic beneficial effect on the morphology and, hence, capacity retention of NiCl$_2$ electrode during cycling.
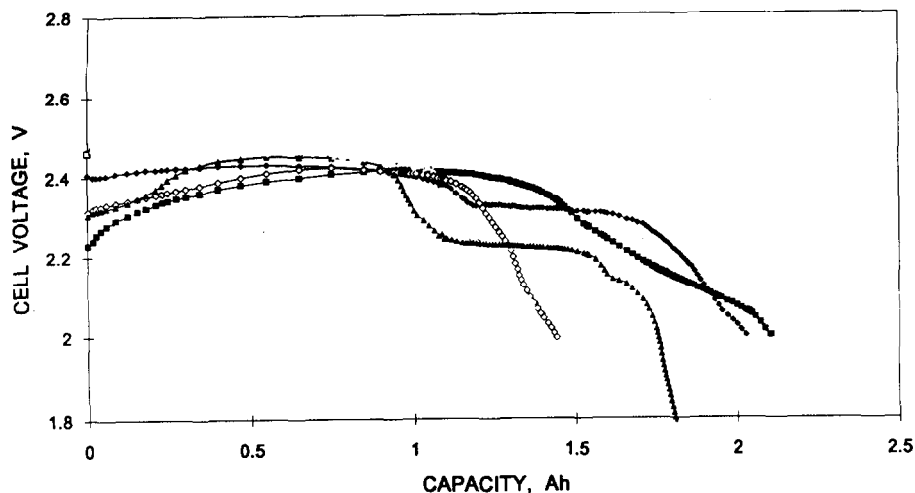
Fig. 9. Discharges curves of 2-Ah 'loose sintered' $NiCl_2$ electrode in the electrolyte; (■) with no additive; (♦) with 10 wt.% cobalt; (◇) with 10 wt.% manganese, and (▲) with 10 wt.% iron.
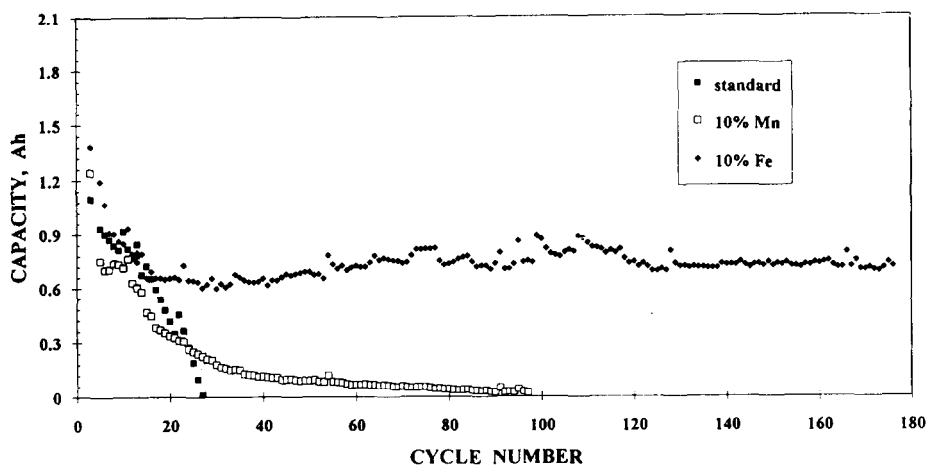

Fig. 10. Variation of capacity during cycling at 10-h rate of 2-Ah 'loose-sintered' $NiCl_2$ electrode in the electrolyte: (■) with no additive; (□) with 10 wt.% manganese, and (♦) with 10 wt.% iron.

Summary

The methods of fabrication of $NiCl_2$ electrode have been optimized to improve its porosity and enhance its conversion efficiency. The charging process has been identified to be a slow process, strongly affected by the electrode porosity. Loose sintered electrodes accordingly show high conversion efficiencies. Foil electrode fabricated with a binder prior to sintering has high surface-area and exhibits high conversion efficiency.

The capacity of the $NiCl_2$ electrode decreases rapidly to $\sim 50\%$ of the initial value within 20 cycles. The beneficial effect of the sulfur additive to the electrolyte on this capacity decline has been demonstrated. From SEM studies, it has been verified that the growth in the grain size during cycling (agglomeration) is responsible for the capacity decline and can be alleviated with the sulfur addition. The optimum (minimum) amount of sulfur additive is in the range of 0.5 to 1.0 wt.%. Addition of transition metals, especially iron and manganese also appears to provide some degree of protection against such rapid capacity fall, though the effect is not as prominent as with sulfur.

Acknowledgements

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