

Sodium–metal chloride battery research at the Jet Propulsion Laboratory (JPL)

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Abstract

Sodium–metal chloride batteries have certain distinct advantages over sodium–sulfur batteries such as increased safety, inherent overcharge capability and lower operating temperatures. Two systems, i.e. Na/FeCl₂ and Na/NiCl₂ were developed extensively elsewhere and evaluated for various applications including electric vehicles and space. Their performance has been very encouraging and prompted a detailed fundamental study on these cathodes here at the Jet Propulsion Laboratory. A brief review of our studies on these new cathode materials is presented here. The initial efforts focussed on the methods of fabrication of the electrodes and their electrochemical characterization. Subsequent studies were aimed at establishing the reaction mechanism, determining the kinetics and identifying the rate-limiting processes in the reduction of metal chloride cathodes. Nickel chloride emerged from these studies as the most promising candidate material and was taken up for further detailed study on its passivation—a rate limiting process—under different experimental conditions. Also, the feasibility of using copper chloride, which is expected to have higher energy density, has been assessed. Based on the criteria established from the voltammetric response of FeCl₂, NiCl₂ and CuCl₂, several other transition metal chlorides were screened. Of these, molybdenum and cobalt chlorides appear promising.

Introduction

The disclosures by Coetzer *et al.* [1, 2] on the use of transition metal chlorides in chloroaluminate melts as positive electrodes in rechargeable sodium batteries have generated a wide interest in the sodium–metal chloride battery systems at various laboratories around the world [3–6]. These battery systems have attractive electrochemical characteristics such as high voltages, high energy and power densities and a long cycle life. Besides, some of the problems often encountered with the sulfur cathode in Na/S batteries are noticeably absent in these systems, making them viable alternatives to Na/S batteries in several applications.

The advantages stem mainly from the way these systems are configured. A Na/MCl₂ cell consists of a solid (insoluble) transition metal chloride in NaAlCl₄ electrolyte separated from the anode (molten sodium) by a Na⁺ ion conducting solid electrolyte (beta alumina ceramic). Some of these advantages are: (i) about 100° lower operating temperatures, (ii) reduced corrosion by

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the catholyte, (iii) increased safety during internal shorts or thermal excursions, (iv) tolerance to overcharge and overdischarge and (v) ease of fabrication in the discharged state with little elemental Na. Not surprisingly, sodium-metal chloride batteries, aided by the above attractive features, are being considered for various applications including load leveling and electric vehicles. Both Na/FeCl₂ and Na/NiCl₂ batteries have been developed in 40–100 A h sizes for electric vehicles application [7]. Further, Na/NiCl₂ batteries are currently being successfully evaluated for GEO and LEO space applications [8].

Considering the promise the Na-MCl₂ battery systems hold for space applications, a programme has been initiated at the Jet Propulsion Laboratory to evaluate these systems for NASA's future missions. The program has hitherto focussed on gaining a fundamental understanding of the electrochemistry of the metal chloride cathodes to augment the developmental effort being pursued elsewhere in the U.S.A. and other countries. In this paper, a brief review of such studies carried out on different metal chlorides is presented.

Experimental

Various methods of fabricating the metal chloride electrodes have been examined. These methods include: (i) hot pressing powders of NaCl and a transition metal with a Teflon binder (stable below 250 °C) to obtain electrodes in the discharged state; (ii) impregnation of a metal chloride in a sintered matrix of the same or nobler metal; and (iii) cosintering of pressed powders of NaCl and a transition metal at 800 °C under argon atmosphere for 6–8 h to obtain the electrodes in the discharged state. The impregnation method has the advantage of providing a suitable morphology for extended cycle life, i.e. the active material is pocketed in the pores of the plaque as in Ni-Cd batteries. In the cosintering method, however, oxidation of the grid is likely as well thus reducing its mechanical integrity during cycling. For the single electrode studies aimed at obtaining fundamental understanding of the metal chloride cathodes, the metal chloride is formed on the metal wire electrode from an *in situ* oxidation in the electrolyte. Other experimental conditions are similar to those reported in our earlier communications [9–14].

Results and discussion

Before embarking on the detailed fundamental studies, initial experiments were focussed on the electrochemical characterization of the metal chlorides, i.e. mainly on the discharge behavior, rechargeability, rate-limiting processes etc. Three metal chlorides, FeCl₂, NiCl₂ and CuCl₂, were chosen for these studies. As mentioned above, FeCl₂ and NiCl₂ have been extensively developed elsewhere. Copper chloride, on the other hand, has not been studied much and was included in this programme with an expectation that its voltage (as well as energy density) would be higher than FeCl₂ and even NiCl₂.

Charge-discharge behavior

The charge-discharge curves of FeCl_2 electrodes, formed by cosintering of Fe and NaCl, and NiCl_2 and CuCl_2 electrodes formed by impregnation (Figs. 2-5 in ref. 9) illustrate the high coulombic yields and good reversibility of these cathodes. Both FeCl_2 and NiCl_2 have flat charge-discharge curves in the range of current densities studied ($1-8 \text{ mA/cm}^2$). Copper chloride, on the other hand, exhibits a higher voltage than FeCl_2 and NiCl_2 but sloping charge-discharge curves, suggesting the possible formation of monovalent copper during reduction of CuCl_2 . CuCl_2 appeared to be chemically stable in NaAlCl_4 electrolyte, which is an essential requirement for a successful operation of the metal chloride cathode in the above sodium batteries.

Polarization studies on sintered electrodes

d.c. Linear polarization studies were performed on the sintered metal chloride electrodes to determine the exchange current densities for their reduction (Fig. 7 in ref. 9 and Fig. 1 in ref. 10). The exchange current densities are in the range of $1-2 \text{ mA/cm}^2$ for NiCl_2 and FeCl_2 and $0-1 \text{ mA/cm}^2$ for CuCl_2 . The values are in good agreement with those derived from the potentiodynamic polarization data. The potentiodynamic polarization curves also show mass transfer effects, evident from limiting currents, in the reduction of metal chlorides. Furthermore, the Tafel plots of NiCl_2 and CuCl_2 contain discontinuities during reduction, which, in the case of CuCl_2 , may be due to the possible formation of monovalent copper. In the case of NiCl_2 , these discontinuities may be attributed to a kinetic effect (described later on as passivation) by the discharge products, especially NaCl. Due to these kinetic effects, the NiCl_2 electrode exhibits lower exchange currents at lower states of charge.

a.c. Impedance studies on FeCl_2 and NiCl_2 reveal single charge transfer steps with exchange current densities comparable to those derived from d.c. polarization data. The complex impedance plots of CuCl_2 , on the other hand, contain a second relaxation loop especially at lower potentials which may be related to the formation of monovalent copper during the reduction of CuCl_2 .

Single-electrode studies

Single-electrode studies were performed on transition metal wire electrodes in NaAlCl_4 electrolyte with an aluminum reference electrode (1.643 V versus Na) and a nickel foil counter electrode in a pyrex cell. These studies were aimed at verifying the reversibility, establishing the reaction mechanisms, determining accurately the rate parameters and identifying the rate limiting processes in the electrode reactions [11]. These studies broadly include cyclic voltammetry, d.c. polarization and a.c. impedance.

The cyclic voltammograms of Ni (Fig. 1) consist of sharp and symmetric peaks both during oxidation and reduction, implying a high degree of reversibility for this system. A single peak is observed during oxidation as well as reduction with a peak splitting close to 48 mV expected for a two-

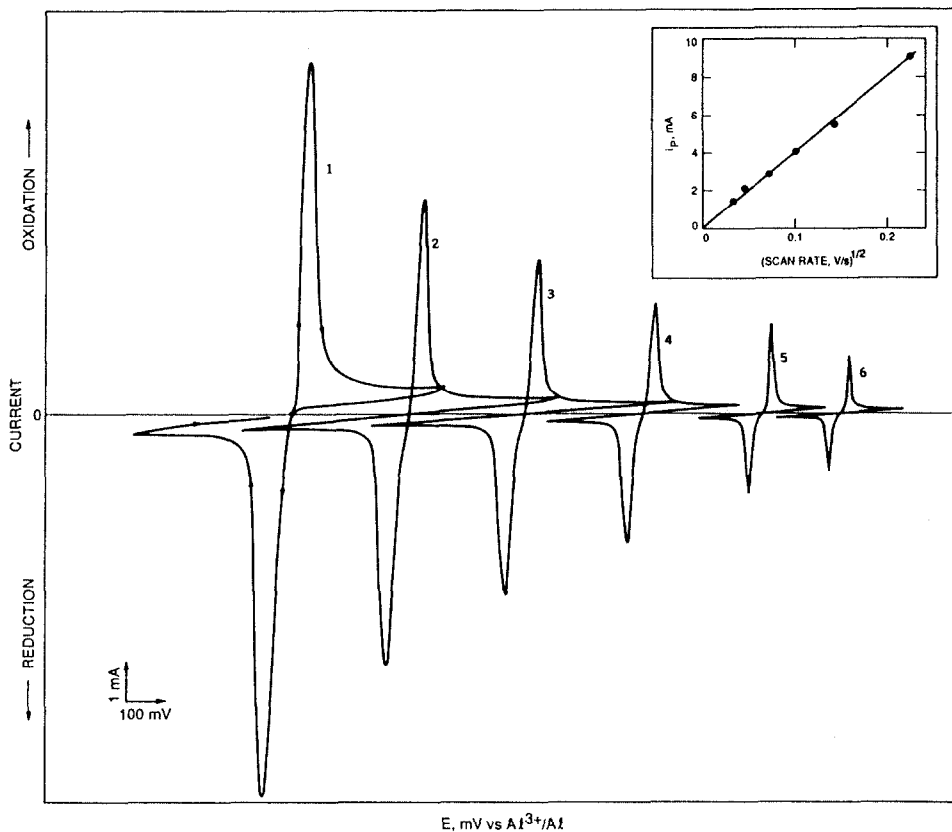


Fig. 1. Cyclic voltammograms of Ni electrode (area: 0.06 cm^2) in NaAlCl_4 at 220°C at different scan rates: 1, 50; 2, 20; 3, 10; 4, 5; 5, 2; 6, 1 mV/s . Peak current varies linearly with the square root of scan rate.

electron reaction, which is consistent with the phase diagram of NiCl_2 , Ni and NaCl. The peak current varies linearly with the square root of scan rate implying mass transfer control over the reaction. The above voltammetric behavior is explained in terms of deposition of the oxidation product, by virtue of its insolubility in the electrolyte, over the electrode manifesting itself in a mass-transfer limited situation. From the slope of the peak current against $(\text{scan rate})^{1/2}$, the diffusion coefficient for Ni^{2+} ions across the layers of NiCl_2 deposited was estimated as $4.5 \times 10^{-8} \text{ cm}^2/\text{s}$. The cyclic voltammograms of Fe (Fig. 2) have symmetric, but broad peaks splitting into two peaks at slower scan rates. The peak splitting is 84 mV, which is expected for two single-electron transfer steps reported to be apart by 12 mV in the reduction of FeCl_2 . The peak currents once again vary linearly with the square root of the scan rate suggesting mass transfer controlled kinetics. The diffusion coefficient for Fe^{2+} across FeCl_2 layers on the electrode was estimated from the slope of peak current against $(\text{scan rate})^{1/2}$ to be

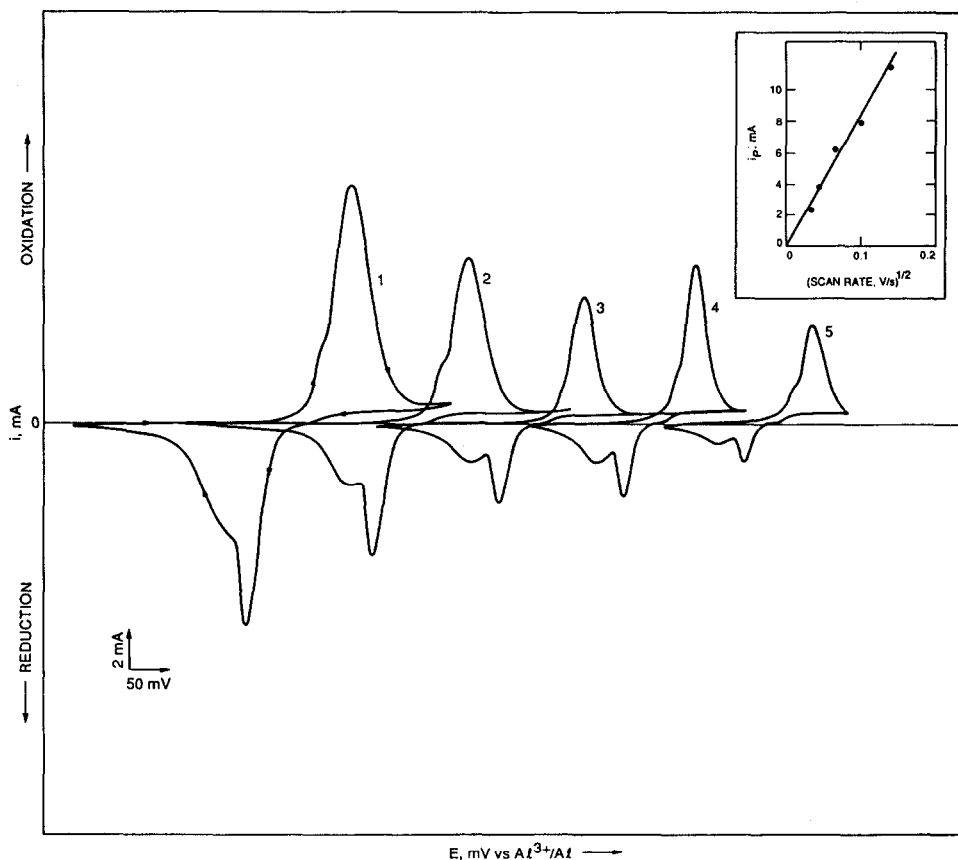


Fig. 2. Cyclic voltammograms of Fe electrode (area: 0.05 cm^2) in NaAlCl_4 at $220 \text{ }^\circ\text{C}$ at scan rates: 1, 20; 2, 10; 3, 5; 4, 2; 5, 1 mV/s. Scale on the y axis is 1 mA/cm (reduced to half for curves 4 and 5). Peak current is again proportional to the square root of the scan rate.

$5.2 \times 10^{-8} \text{ cm}^2/\text{s}$. The voltammograms of Cu show expected higher voltages, but also poor reversibility evident from smaller reduction peaks. Also, the voltammograms contain two peaks; the products formed in the second step possibly monovalent copper, appear to be soluble in the electrolyte. This is further confirmed by the presence of dissolved copper in the electrolyte of a Na-CuCl₂ laboratory test cell, especially when the charging is extended beyond the first step (2.83 V versus Na). The reversibility of CuCl₂ improves if the oxidation is limited to the first step [12].

From the cyclic voltammetric behavior of FeCl₂ and NiCl₂, certain criteria have been established to predict the feasibility of using a metal chloride as cathode material in sodium batteries [13]. These criteria include a low oxidation current subsequent to the peak, implying low solubility for the chloride, and symmetry in shape and size between the oxidation and reduction peaks even at low scan rates. Using these criteria, several transition metal

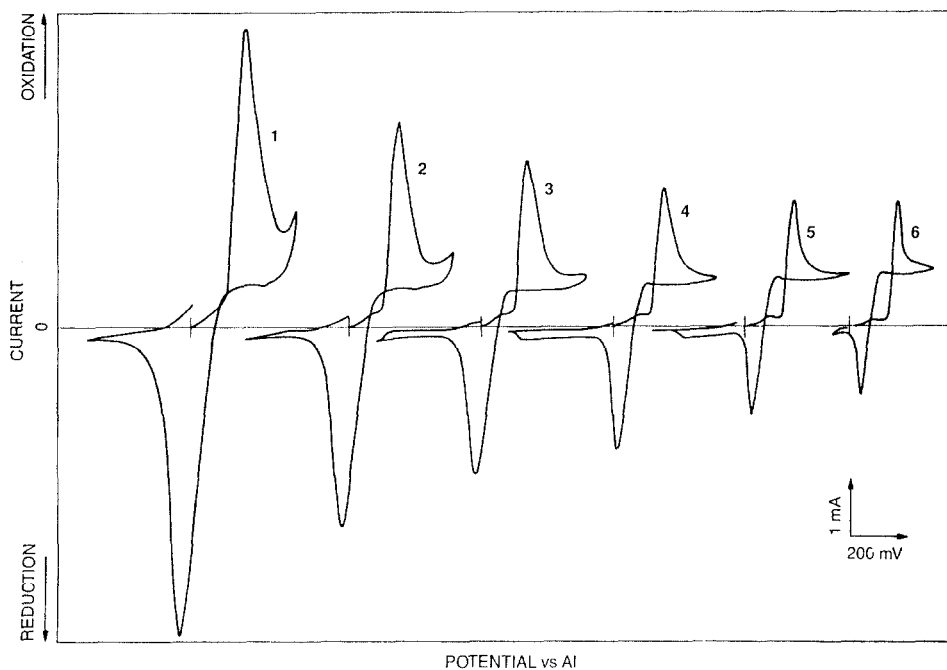


Fig. 3. Cyclic voltammograms of Co (E_0 : 870 mV vs. Al) in NaAlCl₄ at 250 °C at different scan rates: 1, 50; 2, 20; 3, 10; 4, 5; 5, 2; 6, 1 mV/s.

chlorides including vanadium, cobalt, chromium, manganese, molybdenum and silver have been screened. Cobalt (Fig. 3) and molybdenum (Fig. 4) appear to meet those requirements, with the latter also showing promise as a stable current collector for FeCl₂ and NiCl₂ electrodes.

d.c. Micropolarization studies carried out on NiCl₂ and FeCl₂ wire electrodes gave more accurate exchange current densities of 0.73 and 0.43 mA/cm², respectively. Potentiodynamic polarization curves of NiCl₂ exhibit 'passivation' akin to reactive metal anodes, i.e. the current rises sharply and falls down subsequently (Fig. 5). This passivation behavior is attributed to the deposition of NaCl formed during reduction on the electrode surface causing significant ohmic polarization at such sites. This is in fact responsible for the 'segmented' Tafel behavior observed with sintered NiCl₂ electrodes. This aspect is addressed in more detail later on. The current–potential curve of FeCl₂ shows reduced passivity as compared to NiCl₂, probably due to the intermediates formed during reduction being less resistive than NaCl.

The exchange current density derived from the a.c. impedance data of FeCl₂ is 0.66 mA/cm², in agreement with the values obtained from d.c. data. Furthermore, the diffusion coefficient calculated from the Randles' impedance plot for Fe²⁺ ions across FeCl₂ is 4.4×10^{-8} as compared to 5.2×10^{-8} cm²/s derived from cyclic voltammetric data. The a.c. impedance (Nyquist) plot of NiCl₂ is similar to that of a passive system, e.g. iron in sulfuric acid,

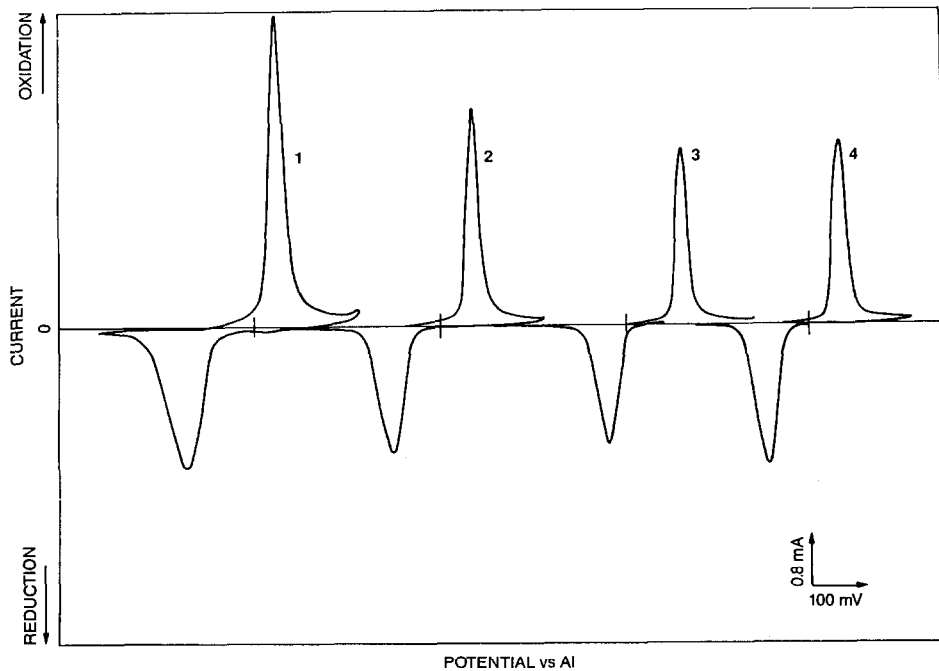


Fig. 4. Cyclic voltammograms of Mo (E_0 : 870 mV vs. Al) in NaAlCl_4 at 250 °C at different scan rates: 1, 50; 2, 20; 3, 10; 4, 5 mV/s (scale on the y axis is doubled for curve 4).

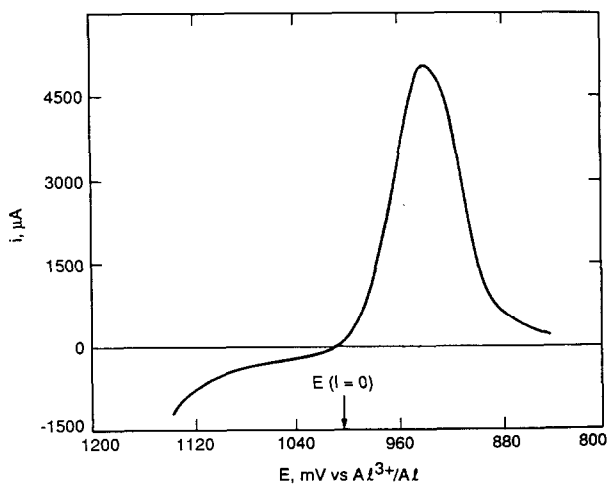


Fig. 5. Typical potentiodynamic polarization curve of NiCl_2 in NaAlCl_4 melt at 250 °C at 1 mV/s, illustrating its tendency to 'passivate' during reduction.

with the relaxation loop bending inward towards the imaginary axis at low frequencies. This characteristic profile (Fig. 6) of the Nyquist plot may serve as a qualitative index for the onset of passivation of NiCl_2 .

Passivation of NiCl_2

From the single electrode studies, NiCl_2 emerged as the candidate cathode material for further study due to its near-ideal reversibility, high exchange current densities, simple reaction mechanism free of intermediates and superior electrochemical characteristics. However, NiCl_2 shows a tendency to passivate during reduction at high current densities, which warrants a proper design of electrode geometry to achieve high power densities. A detailed study on the passivation has been carried out under different experimental conditions [14].

d.c. Micropolarization curves obtained at different states of charge show increasing polarization resistance at low states of charge, implying lower exchange currents. The open-circuit potential, on the other hand, remains the same (Fig. 7). This decrease in the exchange current is explained in terms of a progressive reduction in the active (non-passive) electrochemical area due to deposition of the reduction product NaCl on the electrode. Potentiodynamic polarization curves (Fig. 8) at different states of charge also demonstrate the increasing passivation at lower states of charge as is evident from a sharp decrease in the current at overpotentials exceeding 100 mV.

a.c. Impedance measurements carried out at different states of charge also gave lower exchange currents (Fig. 7) at lower states of charge, in agreement with the results obtained from linear polarization. Also, at lower states of charge, the Nyquist plots exhibit the typical profile characteristic of a passive system, wherein the capacitive component bends inward towards

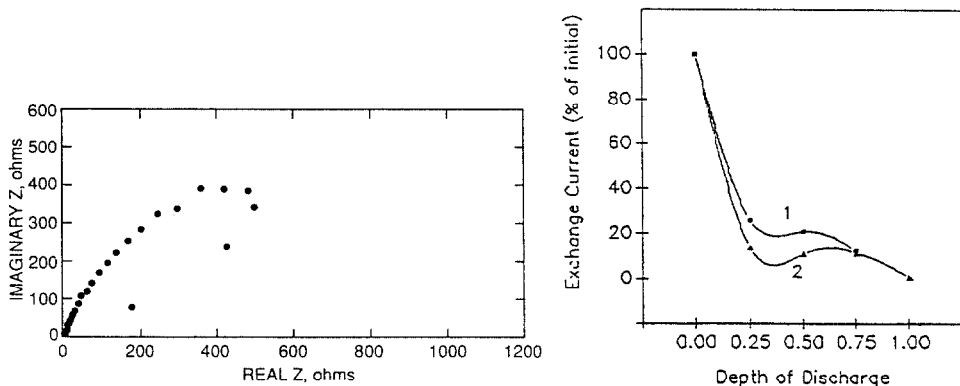


Fig. 6. Nyquist impedance plot of NiCl_2 in NaAlCl_4 at 250°C in the frequency range of 10^5 – 10^{-2} Hz and at an a.c. amplitude of 5 mV.

Fig. 7. Decrease in the exchange currents, derived from d.c. linear polarization (1) and a.c. impedance data (2), with the state of charge of NiCl_2 cathode in Na/NiCl_2 cell at 230°C .

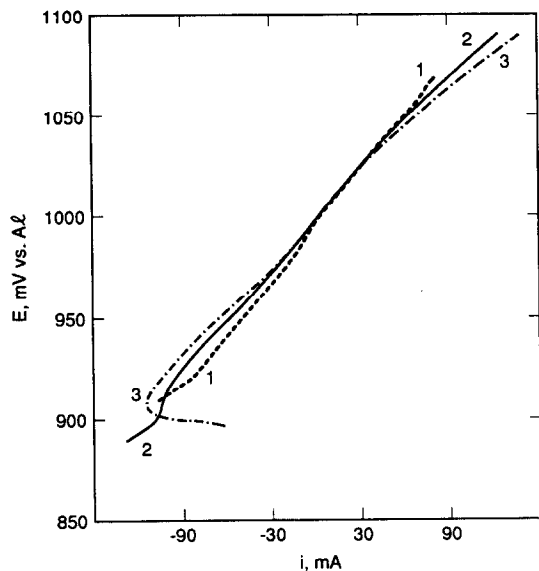


Fig. 8. Current–potential curves of NiCl_2 electrode in Na/NiCl_2 cell at $230\text{ }^\circ\text{C}$ at a slow scan rate of 0.5 mV/s and at different states of charge: 1, 0.75; 2, 0.5; 3, 0.25.

the imaginary axis at low frequencies. a.c. Impedance plots obtained at different electrode potentials suggest that at lower (reduction) potentials, i.e. $<950\text{ mV}$ versus Al, the electrode tends to passivate, as is evident from the characteristic shape of the Nyquist plot. The exchange current appears to decrease with a decrease in electrode potential until 950 mV versus Al after which the electrode has a high impedance due to passivation.

Conclusions

Transition metal chlorides have several attractive features and are viable alternatives to sulfur as positive electrodes in sodium batteries. Our initial studies on metal chloride cathodes were focussed on the methods of fabrication and electrochemical characterization including discharge behavior, rechargeability etc. Detailed fundamental studies carried out in single-electrode configuration gave useful information on the reaction mechanisms, rate parameters and rate-limiting processes. NiCl_2 emerged from our studies as the candidate cathode material for further study and development for NASA's requirements, whereas copper chloride appears to be chemically unstable during extended charge. Among various other metal chlorides screened, cobalt and molybdenum are likely to be successful as cathodes with the latter also having a potential as a stable current collector for NiCl_2 electrodes. The passivation of NiCl_2 , a rate limiting phenomenon, increases at lower states of charge but can be alleviated by a proper electrode design or, as our recent studies show, by increasing the operating temperature to around $275\text{ }^\circ\text{C}$. Higher operating

temperatures also improve the kinetics, the exchange current increasing by 10% for each 10 °C rise in temperature.

Acknowledgements

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