

ADVANCED RECHARGEABLE SODIUM BATTERIES WITH NOVEL CATHODES

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Summary

Various high energy density rechargeable batteries are being considered for future space applications. Of these, the sodium-sulfur battery is one of the leading candidates. The primary advantage is the high energy density (760 W h kg^{-1} theoretical). Energy densities in excess of 180 W h kg^{-1} have been realized in practical batteries. More recently, cathodes other than sulfur are being evaluated. We, at JPL, are evaluating various new cathode materials for use in high energy density sodium batteries for advanced space applications. Our approach is to carry out basic electrochemical studies of these materials in a sodium cell configuration in order to understand their fundamental behaviors. Thus far, our studies have focussed on alternative metal chlorides such as CuCl_2 and organic cathode materials such as TCNE.

Introduction

Rechargeable batteries play a significant role in NASA's space programs, including planetary missions and satellite applications such as Geosynchronous Earth Orbit (GEO) and Low Earth Orbit (LEO) missions. There is an increasing need for a lightweight, high energy battery with long active and cycle lives. Typically, the efforts at various organizations are aimed at developing a batteries system with an energy density $\geq 200 \text{ W h kg}^{-1}$ at power densities $\geq 100 \text{ W kg}^{-1}$, cycle life of 1000 cycles and active life of ten years. Interest for many years has been focussed on the sodium-sulfur battery, which has a high formula energy density ($\sim 750 \text{ W h kg}^{-1}$), a good portion of which has been realized in practical cells for several hundreds of charge/discharge cycles [1]. The battery typically operates at $300 - 400^\circ \text{C}$ where the β'' -alumina solid electrolyte (BASE) is highly conductive to sodium ions, allowing high power densities to be drawn from the battery. Together with these advantages, there are certain deterrent factors associated with the use of the sodium-sulfur battery which partly protracted its devel-

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opment. Dell *et al.* [2] have given an excellent account of the status of the Na-S battery in their recent review. Many of these operational and safety problems stem from the sulfur electrode, *e.g.*, the excessively corrosive nature of the discharge product, sodium polysulfide, towards steels, the high vapor pressure of liquid sulfur above 700 °C, the possible degradation of BASE in polysulfide melts [3], the insulating nature of liquid sulfur, in particular the way in which it isolates regions of BASE during recharge, etc. Alternatives to liquid sulfur cathodes are therefore being sought and there are some examples in the literature based on fused salt electrolytes [4 - 6]. In this paper, we review our studies on alternative organic and inorganic cathodes in sodium batteries. In both cases, the cell contains sodium tetrachloroaluminate as the secondary molten electrolyte and BASE as primary electrolyte.

Carbonitriles are a class of relatively stable organic compounds that have high reduction potentials and energy densities. Tetracyanoethylene (TCNE) in particular has an energy density of $\sim 620 \text{ W h kg}^{-1}$ at a high potential of $\sim 3.0 \text{ V}$ versus Na^+/Na and a low melting point. Therefore, TCNE has been examined as a possible liquid cathode in sodium batteries. Among the inorganic cathode materials, transition metal dichlorides (*e.g.*, FeCl_2 and NiCl_2) are gaining increasing attention as solid, insoluble rechargeable cathodes in place of liquid sulfur [8 - 11]. These systems can operate at lower temperatures, $\geq 170 \text{ }^\circ\text{C}$, where the corrosion problems are proportionately less severe. The safety problem is considerably reduced due to the inherent sluggish kinetics of the chemical reaction between liquid sodium and NaAlCl_4 molten electrolyte in the event of ceramic failure [12]. Further, the molten electrolyte remains invariant during charge/discharge, preventing polarization losses and localized high current densities on the BASE surface. High energy densities, $\sim 150 \text{ W h kg}^{-1}$, and long cycle life have been demonstrated with ferrous chloride, and more recently with nickel chlorides. We summarize below our electrochemical studies on the ferrous chloride and nickel chloride cathodes and also on another promising metal chloride, copper chloride.

Experimental

The experimental cell adopted for these studies is described in detail in ref. 7. The cell, essentially, has a central-cathode design with a provision to seal the anode half-cell. The cell is heated electrically, with a heating tape wound around a stainless steel tube acting as a container for sodium. For the studies involving TCNE, either Pt or C is used as the positive current collector. Metal chloride positive electrodes were initially fabricated by impregnating commercially available sintered nickel grids (used in Ni-Cd batteries) with the depolarizer by immersing the grid into a concentrated chloride solution. Copper electrodes cannot, however, be made in this manner for long-term studies due to the preferential dissolution of nickel to copper in

the impregnating solution. Perforated copper grids were therefore used to make electrodes in the discharged state either by hot pressing with a binder (Teflon) or by sintering the powders in an inert atmosphere at temperatures below the melting point of NaCl. Conventional electrochemical equipment consisting of an E G and G 273 potentiostat/galvanostat and an E G and G 5301 lock-in amplifier interfaced with an Apple IIe computer were used. a.c. and d.c. measurements were carried out using E G and G a.c. impedance and Softcorr software. Various techniques, such as potentiodynamic polarization, d.c. linear polarization, and a.c. impedance were employed to obtain information on the kinetic parameters of the cathode reactions. Discharge/charge cycling was also carried out galvanostatically in a controlled fashion using the above electrochemical equipment. All the chemicals, TCNE, NaAlCl_4 , NaCl, and metal powder, were of analytical grade and were used as received. BASE tubes were cleaned by etching in hot phosphoric acid. All the cell fabrication operations were carried out in an argon-filled glove box.

Results and discussion

The findings of our studies on TCNE as a cathode material in sodium batteries are described in detail elsewhere [7]. Briefly, TCNE reduces at 3.0 V *versus* Na^+/Na reversibly with a coulombic yield of >60% at 1 mA cm^{-2} on either the Pt or C current collector. Figure 1 gives the typical

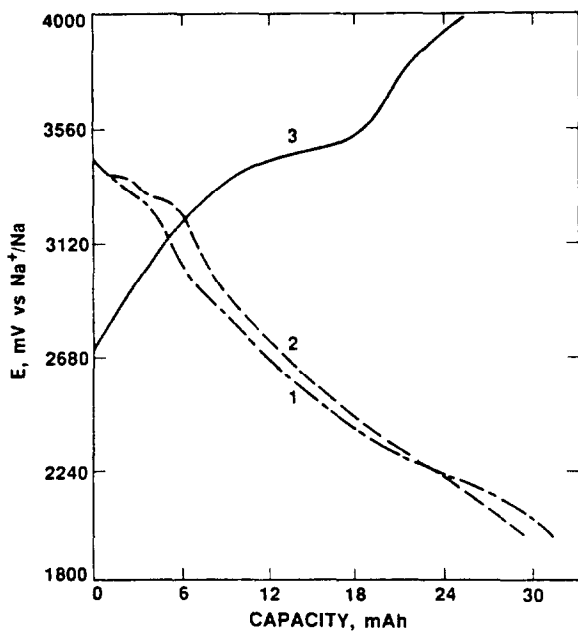


Fig. 1. Typical charge/discharge curves of TCNE (10 wt.%) at 230 °C: 1, Fourth discharge; 2, fifth discharge; 3, charge.

voltage-time curves of TCNE during discharge and charge. The exchange current density on either Pt or C is of the order of 10^{-3} A cm^{-2} in a catholyte containing, typically, 10 wt.% of TCNE. The kinetics of TCNE reduction are essentially governed by the rate of mass transfer in the catholyte, as evidenced from a.c. impedance and d.c. potentiodynamic polarization data. In TCNE-rich catholytes there is a kinetic hindrance to the reduction of TCNE reflected in increased polarization (ohmic, concentration, as well as charge transfer) losses. As a result, the coulombic yield as well as the diffusion coefficient of TCNE decrease with increasing TCNE concentration in the catholyte. The sluggish kinetics at higher TCNE concentrations is related to the degradation processes occurring in TCNE at operating temperatures of ~ 230 °C, forming an adduct. FTIR studies point to a possible polymerization of TCNE under the experimental conditions. Due to the sluggish kinetics at higher TCNE concentrations, it may not be possible to achieve high power densities from TCNE. On the other hand, for medium-to-low power applications, TCNE is a good cathode material, since the electrochemical activity and reversibility of TCNE are retained even after polymerization.

Metal dichloride cathodes

Figure 2 shows the typical charge/discharge curves of an ~ 16 mA h NiCl_2 electrode (made by impregnating NiCl_2 into sintered Ni plaque) at 200 °C and at 2 mA cm^{-2} in the first two test-cycles. The discharge curves, as well as the charging curves, are flat at nominal voltages of 2.56 and 2.63 V

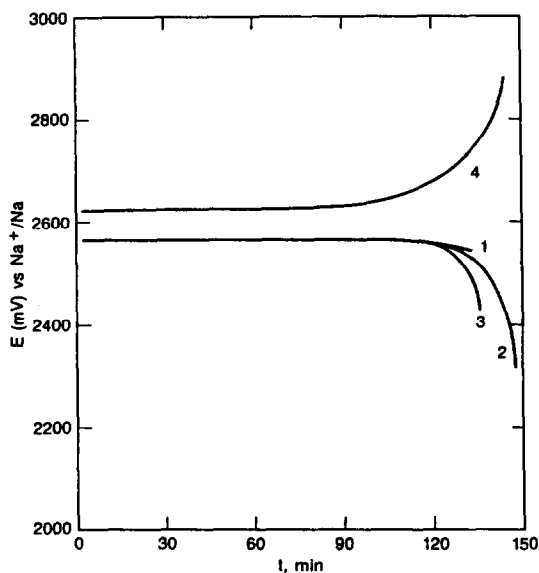


Fig. 2. Typical charge/discharge curves of a 16 mA h electrode at 200 °C during 1, second; 2, third; 3, fourth discharge; 4, charge at 2 mA cm^{-2} .

versus Na^+/Na , respectively. There is not much polarization loss from the open circuit voltage of 2.59 V.

The coulombic yield is nearly 100% and there is no loss in capacity during cycling in the first few test cycles. Figure 3 illustrates the high rate discharge capability of the electrode. The discharge curves at higher current densities, *i.e.*, 4 mA cm^{-2} and 8 mA cm^{-2} are also flat, with mid-point voltages of 2.54 and 2.5 V and coulombic yields of 98% and 90%, respectively. Ferrous chloride electrodes (made by sintering dry powders of sodium chloride and iron) exhibit a lower operating potential of $\sim 2.3 \text{ V}$, as may be seen from the discharge and charge curves of an $\sim 230 \text{ mA h}$ electrode in Fig. 4. The discharge curve is flat in this case also, with a coulombic yield in excess of 90%. The copper chloride cathode is expected to give a higher voltage than the nickel chloride cathode, from the electrode potentials of Cu^{2+}/Cu and Ni^{2+}/Ni couples. Accordingly, higher energy densities may be possible with copper chloride as compared with ferrous chloride or nickel chloride, especially at high power densities, due to the high electronic conductivity of copper formed in the course of discharge. The essential requirement for the successful operation of a metal chloride cathode in the above sodium batteries is total insolubility of the chloride in an NaAlCl_4 melt. Analytical studies carried out on the catholyte with CuCl_2 and NiCl_2 revealed no extra dissolution of copper over nickel. Initial studies with copper chloride (electrode made by impregnation of CuCl_2 into sintered Ni plaque) show a higher

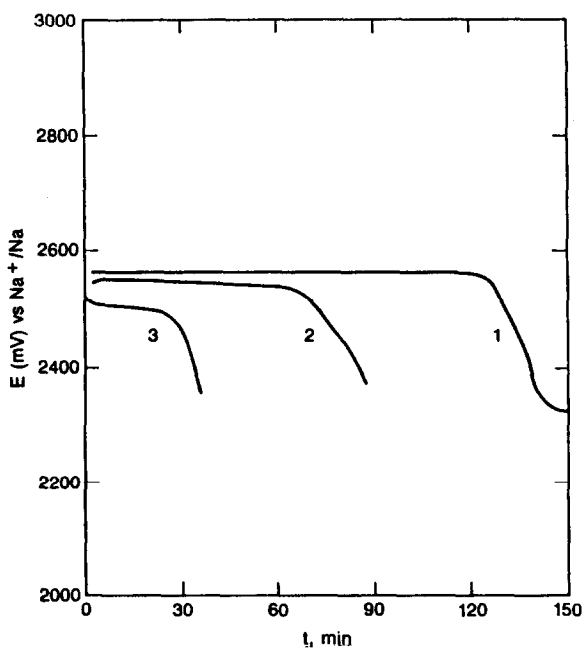


Fig. 3. Discharge curves of a 16 mA h NiCl_2 electrode at 200°C and at current density of 1, 2 mA cm^{-2} ; 2, 4 mA cm^{-2} ; 3, 8 mA cm^{-2} .

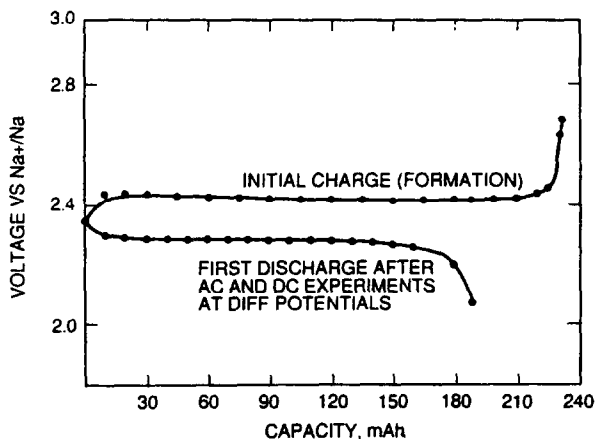


Fig. 4. Initial charge/discharge curves of FeCl_2 cathode.

operating voltage than NiCl_2 or FeCl_2 (Fig. 5). The discharge (as well as charging) curve is, however, not flat in this case, as with FeCl_2 or NiCl_2 , which may be due to the mechanism of reduction being different, with the possible formation of a monovalent copper.

D.C. polarization studies were carried out on these cathode materials to obtain information on the kinetics of their reduction. The potentiodynamic polarization curves of NiCl_2 , FeCl_2 , and CuCl_2 (Fig. 6) illustrate the high rate

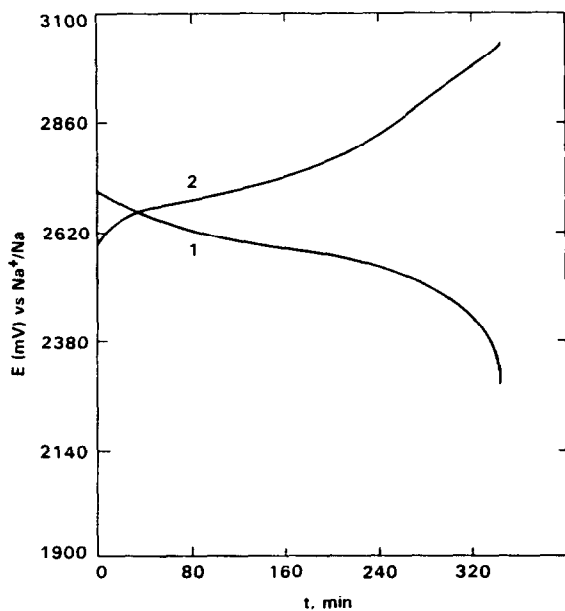


Fig. 5. Charge/discharge curves of CuCl_2 electrode (made by impregnating CuCl_2 into a sintered nickel grid) at 200°C .

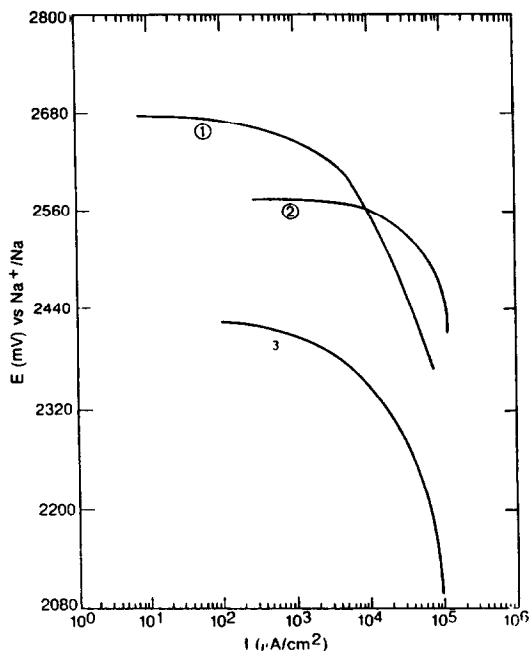


Fig. 6. Potentiodynamic polarization curves of 1, CuCl_2 ; 2, NiCl_2 ; 3, FeCl_2 .

capability of these electrodes. Mass transfer effects exist at high discharge rates, interfering with the charge transfer processes, due to which limiting currents are observed at high overpotentials ≥ 300 mV. The limiting currents may be due to relatively slow diffusion processes inside the porous cathode. Nevertheless, the limiting current densities are reasonably high and are of the order of 15 - 25 mA cm^{-2} . The charge transfer kinetics appear to be rapid, as evidenced by high exchange current densities of 2 mA cm^{-2} , 0.65 mA cm^{-2} and 0.4 mA cm^{-2} for NiCl_2 , FeCl_2 , and CuCl_2 , respectively, based on the geometric areas of these electrodes. Linear polarization experiments (*i.e.*, at low perturbations) were also carried out to derive similar information on the exchange current densities. The current-potential curves at these potentials are linear (*e.g.*, FeCl_2 in Fig. 7), the slopes of which give the polarization resistances. The exchange current densities thus obtained are 4.6 mA cm^{-2} , 1.5 mA cm^{-2} and 0.39 mA cm^{-2} for NiCl_2 , FeCl_2 , and CuCl_2 , respectively.

The complex plane impedance spectrum of NiCl_2 (Fig. 8) shows a large inductance at high frequencies, not shown in the Figure attributed to the porous nickel grid, and a low frequency semi-circle ascribed to charge transfer kinetics. The exchange current density calculated therefrom is 6.9 mA cm^{-2} . There is no evidence of diffusional impedance in the frequency range studied (*i.e.*, ≥ 0.01 Hz). The complex plane impedance spectrum of the CuCl_2 (sintered) electrode, on the other hand, contains two relaxation loops. The exchange current density evaluated from the first relaxation loop is 0.9 mA cm^{-2} . It is, however, not yet clear whether the second relaxation loop is

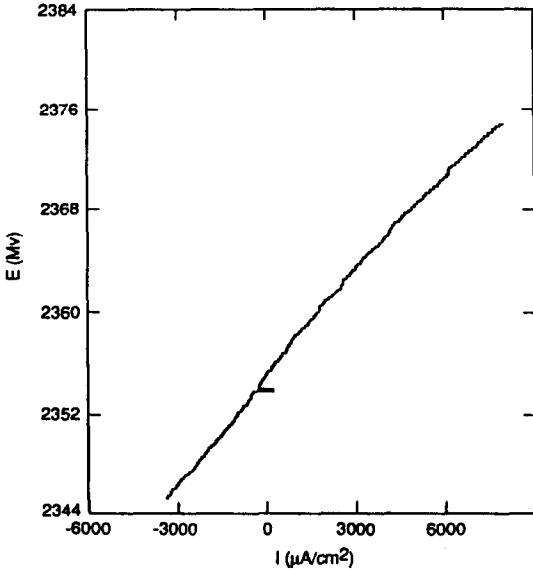


Fig. 7. Linear polarization curve for FeCl_2 from which an exchange current density of 1.5 mA cm^{-2} is calculated.

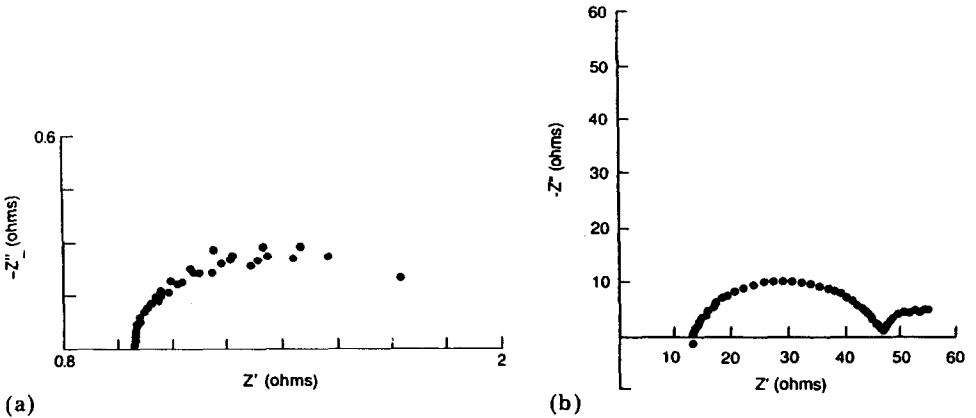


Fig. 8. Complex plane impedance of (a) NiCl_2 ; (b) CuCl_2 .

related to the formation, if any, of monovalent copper during the reduction of CuCl_2 .

Conclusions

Among the cathode materials studied at JPL as alternatives to the sulfur cathode in sodium batteries, TCNE is suitable for low-to-medium power applications. Metal dichloride cathodes, on the other hand, can deliver

energy densities comparable with sodium-sulfur batteries at high power densities without many of the operational and safety problems associated with the use of sodium-sulfur batteries, and are thus suitable for various applications including space, EV load-levelling, etc. The electrochemical studies carried out so far indicate high exchange current densities for the reduction of these cathodes.

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