

Short Communication

A New High Energy Density Battery System

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An advanced high energy density battery system has been developed based upon a novel positive electrode which comprises a transition metal in combination with a molten salt, NaAlCl_4 , and a β -alumina solid electrolyte. In one of its simplest forms, the only active ingredients are iron and sodium chloride.

Despite major efforts in research and development during the past decade no advanced battery is yet commercially available.

Electrochemical systems are often judged by performance only, but it is frequently high materials cost and adverse safety characteristics that make a system non-viable. In particular, the cost goals required for traction and load levelling applications eliminate many electrochemical systems.

This brief communication is the first disclosure in the scientific literature of a novel electrochemical system that has the potential of meeting all the requirements for viability. Since its inception in the late 1970s progress has been rapid. Full size batteries have been tested.

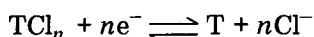
The new battery is similar in physical form to a sodium/sulphur battery in that it uses a β -alumina solid electrolyte. Its cell chemistry, however, is different, with cells which are safe and substantially corrosion-free.

The discharged positive electrode was originally based on a specific class of transition metal compounds known as the intermediate hard metals [1]. This class involves the transition metals (Cr, Mn, Fe, Co, Ni) in combination with certain non-metals such as carbon and boron. These electrodes are chlorinated when in the charged state. The range of discharged electrodes has since been extended to cover the above five metals in elemental form [2, 3].

The positive electrode incorporates molten NaAlCl_4 , saturated with NaCl at the cell operating temperature. A crucial feature of the positive electrode reaction is that it requires the electrochemically active species to be effectively insoluble in the molten salt electrolyte. This contrasts with cells where dissolution of the active species occurs in the positive electrode [4, 5]; it has a true solid state cathode and a solid-liquid interface. The

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electrochemically active material (*e.g.*, FeCl_2) must always remain closely associated with, or "pinned" to, the electronically conductive backbone matrix, which can be unreacted metal itself or carbon, if desired. The cathodic reaction can be written as:



where T is a transition metal and n an oxidation state in which the transition metal ion shows minimal solubility in the molten salt electrolyte.

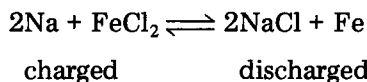
Typical cell configurations can be written:

| | | | | | |
|-----|--------|---------------------|-----------------------|-------------------|-----------|
| (a) | Na/ | β'' -alumina/ | NaAlCl ₄ / | FeCl ₂ | (Fe, C) |
| (b) | Na/ | β'' -alumina/ | NaAlCl ₄ / | NiCl ₂ | (Ni, C) |
| | liquid | solid | liquid | solid | current |
| | anode | electrolyte | electrolyte | cathode | collector |

The anode is liquid, metallic sodium, and a solid ceramic electrolyte (β -alumina) is used as a separator for the materials in the anode and cathode compartments, respectively. There are, therefore, two distinct sodium ion conducting electrolytes in the cell, namely, the molten NaAlCl₄ and β -alumina.

The use of an NaAlCl₄ electrolyte permits the normal battery operating temperature to be about 250 °C. Simple methods of thermal management may be readily used (*e.g.*, flameless catalytic combustion techniques [6]). Both electrodes and the liquid electrolyte have low vapour pressures, even at temperatures well above the cell operating temperature, and therefore no high pressures are generated inside the cell. No safety problems have been encountered with these cells, even in the event of massive β -alumina failure [7]. This system allows considerable freedom in cell and battery design. Cells with a capacity of 1 kW h are quite feasible. A schematic cell layout is shown in Fig. 1.

A simplified cell reaction can be written as:



The open circuit voltage is 2.35 for iron (and 2.59 for nickel) at an operating temperature of 250 °C with a theoretical energy density of more than 700 W h kg⁻¹. Typical discharge curves at various rates are shown in Fig. 2.

The high charge/discharge rates which could be achieved were unexpected: both FeCl₂ and NaCl are known to be poor electronic conductors and both NaCl and FeCl₂ are effectively insoluble in NaAlCl₄ at 250 °C — thereby indicating that the reaction mechanism is likely to be more complex than suggested by the simple reaction above. Investigation into the nature of this mechanism is continuing.

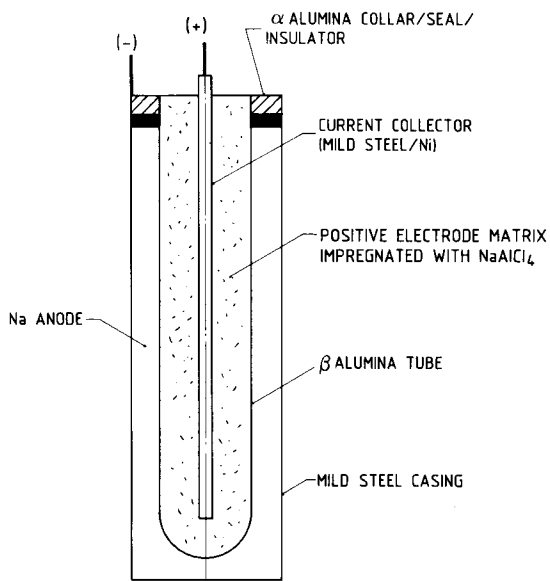


Fig. 1. Schematic diagram of cell.

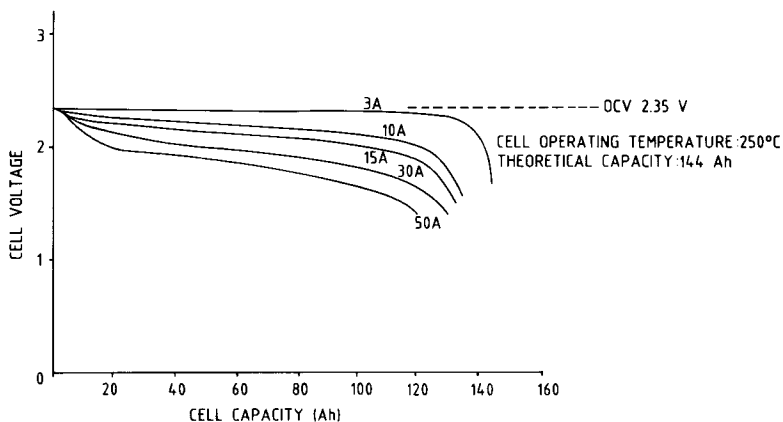


Fig. 2. Typical discharge curves for the Na/FeCl₂ system at 250 °C.

Cells incorporating iron cathodes have a tendency to increase in resistance when cycled. It has been found that small additions of NaF to the melt effectively eliminate this problem [8].

Cells have been cycled for over one thousand cycles at moderate rates ($C/5$) without serious degradation [7].

When cells are loaded in the charged state it entails the partial chlorination of a porous iron matrix to the divalent state and the use of metallic sodium [2, 3].

Electrochemical cells based on positive electrodes of the above type have performed extremely well and practical specific energy and power figures (for cells) of $130 \text{ W h kg}^{-1}(C/5)$ and $100 \text{ W kg}^{-1}(\text{peak})$, respectively, have been achieved.

Multi-kW h batteries have been used successfully to power electric cars, thus demonstrating the potential of the system. The cheap and abundant raw materials used, in conjunction with the extremely good performance figures achieved, make this system a most attractive candidate for commercial applications such as vehicle traction, load levelling and aerospace.

Development of this battery is being actively pursued.

Acknowledgements

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