

SODIUM METAL CHLORIDE BATTERY - AN OVERVIEW

M KAMALUDEEN, N G RENGANATHAN M RAJU P L SANKAR AND A VISUVASAM

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

[Received: 1992 February; Accepted: 1992 March]

The two sodium metal chloride systems namely NiCl_2 , FeCl_2 have been described. Method of forming positive electrode has been indicated. Constructional, operational and safety advantages of zebra system, the problem areas and their remedies have been discussed.

Key words: Zebra cells - Sodium-metal chloride battery

INTRODUCTION

In 1986 Coetzer has demonstrated a new medium temperature secondary system called Zebra batteries. This new system seems to be a better candidate for electric vehicle (EV) traction and load levelling operation, as compared with conventional Na S batteries, [1,2]. In common with Na S cell, these cells also use beta alumina solid electrolyte-cum-separator, but instead of sulphur electrode, the positive electrode, the positive electrode is composed of chloride of transition metals (Fe, Ni, Cu, Mo, Cr, Co, Mn, etc) especially FeCl_2 , or NiCl_2 impregnated in a saturated basic melt of NaAlCl_4 in which FeCl_2 or NiCl_2 are effectively insoluble, [1].

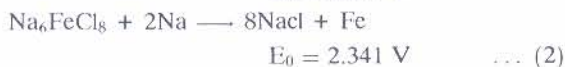
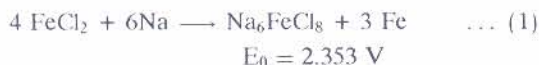
The prospects, advantages and potentialities of Na FeCl_2 and Na NiCl_2 batteries are discussed in this communication.

Zebra cells can be represented by two configurations, as the positive metal chloride electrode may be located either inside or outside the beta alumina tube as shown in Fig. 1.

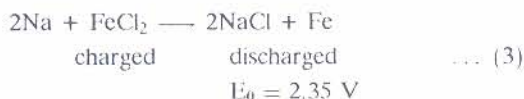
Na- FeCl_2 system

This system is represented as liq.Na/beta alumina// FeCl_2 - NaAlCl_4 /Fe.

The electrode reaction is given by



Overall [3]



Thus in the charged state, the positive electrode consists of a porous Fe matrix which has been partially chlorinated to FeCl_2 . This matrix is immersed in and impregnated with basic NaAlCl_4 which is prepared by melting equimolar mixture of NaCl and AlCl_3 followed by purification by pre-electrolysis and filtration. On subsequent discharge of the cell, Na^+ ions pass through the beta alumina and NaAlCl_4 to reduce the FeCl_2 to Fe, forming NaCl in the process. In this cell, cathode reactants viz. Fe, FeCl_2 , are insoluble in NaAlCl_4 electrolyte.

Na- NiCl_2 system

liq. Na/beta alumina/ NiCl_2 - NaAlCl_4 /Ni

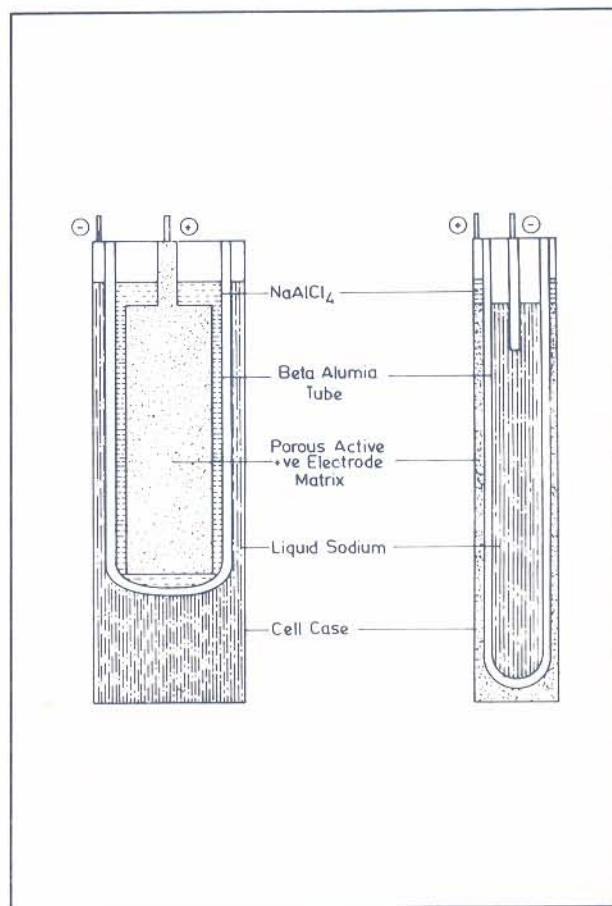
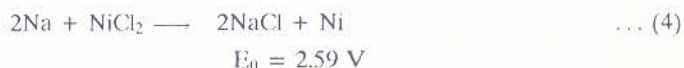


Fig. 1: Zebra cell (a) Positive metal chloride inside the beta alumina tube (b) Positive metal chloride outside the beta alumina tube

The electrode reaction is



charged Discharged

Similar to the Na- FeCl_2 system, here also the Na^+ ions pass through beta alumina and NaAlCl_4 during discharge to reduce

NiCl₂ to Ni + NaCl. In the charged state, the positive electrode consists of a porous Ni electrode which has been partially chlorinated to NiCl₂ and impregnated in basic NaAlCl₄ melt.

In both the cases, a small amount of Na is taken as negative electrode to facilitate charging. Cells are charged and discharged at constant current to 3V and 1.8V respectively. NaAlCl₄ offers a useful electrochemical window for a span of 2.1 V between Al deposition at the end of discharge (1.6 V) and Cl₂ gas evolution at the top of charge (3.7 V) [4].

From the above electrode reactions, it is quite obvious that the successful development of the Zebra system depends on two key factors: (i) insolubility of the positive metal chloride electrode in NaAlCl₄ melt at the operation temperature. (ii) convenient assembling of cells in the discharged state

Positive electrode forming

The metal chloride electrodes have been prepared in the discharged state by various methods [5].

(a) Powders of transition metal and NaCl are hot pressed with teflon binder.

(b) Pressed powders of transition metal and NaCl are cosintered [1, 2] at 1073K under argon or H₂ atmosphere for 6-8 hours.

(c) A sintered matrix of the transition metal or noble metal is formed and then it is impregnated with chloride.

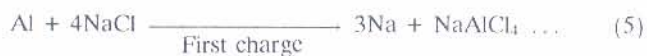
The impregnation method provides suitable morphology for extended cycle life. In the cosintering method, oxidation of the grid is likely to take place and this will reduce its mechanical integrity during cycling.

Zebra systems have several favourable features in the constructional, performance and safety aspects as compared with Na S system.

Constructional

Since the cells are assembled in the discharged state, forming of positive electrode is quite easy. Simple blending of Ni or Fe powder with NaCl powder in the predetermined ratio and packing in the positive electrode compartment with suitable current collecting lead is enough. Presintering of the powder mixture to form electrode may not be necessary. The use of powdered cathode facilitates full utilisation of the electrode compartment avoiding any tolerance problem that occurred with tight fitting sintered electrodes. The choice of powder ratio is also for wider as sinterability is no longer a problem at all.

Cells may be assembled in overdischarged state also. The main advantage of this procedure is that such cells may be assembled with no sodium in the anode compartment. This could be accomplished by the addition of extra Al metal powder with NaCl to the normal discharged mix of NaCl and Ni(Fe). During first charge of such cells, Al and extra NaCl are consumed to produce Na metal according to the reaction



Na formed in the anode compartment by this surplus mix can be retained for further charge-discharge cycles.

Though the two configurations are feasible for both systems, it is better to keep the NiCl₂ inside the beta tube for cost reasons as it necessitates a costly nickel container to hold NiCl₂. In the case of FeCl₂, a less costly mild steel container may find suitable to hold the positive mix.

Operation of the cell

A wide range of operation temperature is possible in Zebra systems [4]. As NiCl₂ forms eutectic with NaCl at 843 K, the upper temperature limit for operation of the Ni system set around 673 K facilitating a wide operating range of 523–673K. Similarly FeCl₂ forms eutectic with NaCl at 674K thus allowing the upper temperature limit of operation around 623 K.

Both systems show higher OCV than NaS system.

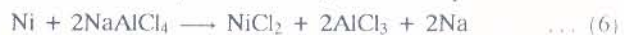
$$E_0 \text{ FeCl}_2 = 2.35 \text{ V}; E_0 \text{ NiCl}_2 = 2.59 \text{ V}$$

$$E_0 \text{ NaS} = 2.08 \text{ V}$$

Nickel system has the advantage of 20% greater power than Fe system since maximum power is proportional to the square of OCV.

Though continued overcharge or overdischarge is undesirable for batteries in general, Zebra system can tolerate these extremes to some extent [1, 2].

During overcharging, any excess Ni present in the positive mix may react with NaAlCl₄ to form NiCl₂ and Na as per the reaction:



During overdischarge, Na is converted into NaCl by reaction with NaAlCl₄



The reversible reaction can be used as an indication for the end of discharge and an overcharge protection.

Tolerance to freeze-thaw cycle is an important feature for high temperature batteries. Recent work on Zebra cells of 40–100Ah capacity with 33–55 mm (dia) beta tubes have shown to be resistant to over 30 thermal cycles and this tolerance is attributed to the nature of the solid NaAlCl₄.

Corrosion of cell case of current collector which is normally encountered in NaS cell, causes a capacity decline and fall in cell life due to the effect of sulphur electrode process and deposition of corrosion products on beta alumina blocking the electrolyte area. Corrosion problem is largely circumvented in Zebra cells because of the low surface area of the cell case or current collector as compared with a large surface area of the active positive electrode. The performance of the cell will not be affected due to the presence of corrosion product viz. metal chloride, with which the electrode is composed of.

As the operating temperature of Zebra cells is below 573 K, a liquid cooling system which is compact and efficient, can be utilised to keep the cell at operating temperature. This is not possible in the case of Na S as the maximum operating temperature of the available liquids is well below 573 K. By virtue of wide temperature of operation of these cells, the built in cooling systems can also be dispensed with. For example, the system operation at 573 K may experience a temperature rise of less than 75 K on deep discharge. The ability to operate safely over a wide range makes thermal management much simple.

Safety

Zebra cells are considered to be more safe than Na S cells.

Even in the case of breach of beta alumina tube due to any thermal, mechanical or electrical failure, the effect will be less severe as compared with Na S cells [6]. This is because of the following reasons: (i) Na does not react with Ni or NaCl. (ii) Na reacts with NaAlCl₄ forming solid products like Al and NaCl which are harmless.

The vapour pressure of these products is < 1 bar at 1073 K while that of Na S cell is > 20 bar at the same temperature.

Aluminium content in the reaction product allows chains of cells to be connected in series without the need for parallel connections, since failed cell will continue to pass current:

Problem Areas & Remedies

In the case of Fe system, it deteriorates if allowed to enter the overcharge region due to the formation of FeCl₃ which is soluble in NaAlCl₄ and beta alumina is also attacked by Fe³⁺ ions. Addition of Ni to Fe (~ 20%) [7] prevents this attack, as the emf. of Na/FeNi cell (2.75V) is higher than that of Ni/NiCl₂ cell (i.e. 2.59V)

Cells incorporating Fe cathodes have the tendency to increase the resistance, when cycled. It has been found that small addition

of NaF to NaAlCl₄ melt effectively eliminates this problem [7]. This may be due to the complex forming ability of fluoride ion with Fe³⁺. Positive electrodes behave extremely well and practical energy and power density of 100 WhKg⁻¹ (c/5) and 100 WKg⁻¹ (peak) respectively have been achieved.[8]. The ratio of Ni to NaCl on optimisation gave an utilisation value of >40% Ni, the remaining provided the electronic conductivity. Electrodes loaded at 0.35 Ah.g⁻¹ of Ni exhibited good capacity retention over several hundred cycles on life testing studies.

It was observed that the capacity retention of earlier cells was poor, reducing by ~ 40% in the first 10 cycles [1, 2]. The capacity loss was shown to be a function of cycling rather than time and the capacity losses being slightly faster at higher temperature. During posts-operative investigation it was identified that grain growth occurs in the Ni metal matrix, leading to the loss of both active surface area and the fine porosity [1, 2]. The cluster of Ni particles had an angular appearance consistent with grain growth from the melt phase. The matrices were very weak and coarse powder with increased grain size which increased with cycle life, temperature and porosity of the original electrode.

Various additives like other halides to the melt was of no influence in reducing the loss in capacity. However small additives of sulphur (1-5 w/o) to NaAlCl₄ or Fe to the Ni matrix cause changes in the morphology of the cathode matrix[9]. Addition of 1-5 w/o S to NaAlCl₄ added at the lower domed end of the beta alumina tube resulted in excellent capacity retention [1, 2, 7].

In S doped Ni cells after 2047 cycles at 573K no damage or Ni penetration on beta alumina was observed. Absence of growth of Ni grain and presence of agglomerates of fine Ni particles would be the reason for capacity retention of the cell. Addition of few % of Fe to Ni matrix cathode has also resulted in good capacity retention due to the absence of grain growth.

Aluminium diffusion bonded seals cannot be made in Zebra cells as aluminium is attacked by NaAlCl₄. So new type of hermetic seals have to be developed specifically for zebra cells [8].

The excellent performance of zebra batteries, in addition to the cheap and abundant raw material, makes the system the most attractive candidate for various commercial applications like EV, traction, utility load levelling and aerospace. EV tested with Zebra batteries is given in the Table I.

TABLE-I: EV tested with Zebra batteries

Year	Organisation	System	Capacity (kWh)	EV	Range (km)
1986	Zebra Power System	Fe	50	Suzuki	252
	Beta Research and Development, UK	Fe	40	Ford	230
					Escort
	Beta Research and Development, UK	Ni	30	Suzuki	130
				Micro bus	
1989-90	Beta Research +	Ni	30	Mercedes	150
	AFG Anglo Battery Holdings.			Benz	70km.h ⁻¹

REFERENCES

1. R J Bones, J Coetzer, R C Galloway and D A Teagle, *J Electrochem Soc*, **134** (1987) 2379
2. R C Galloway, *Brief Communications, ibid*, **134** (1987) 1
3. R J Bones, D A Teagle, S D Brooker, J Lumsdon and F L Cullen, 171st Meeting, Electrochem Soc, Philadelphia, (1987). Abstract No. 553
4. R C Galloway, *J Electrochem Soc*, **134** (1987) 256
5. R V Ratnakumar, A Iattia and G Halpart, *J Power Sources*, **36** (1991) 385
6. A R Tilley and R J Wedlake, *Electr Vehicle Dev*, **6-4** (1987) 119
7. R M Dell and R J Bones, 22nd Intersoc Energy Conversion Eng Conference, Philadelphia Pennsylvania, Aug. 10-14 (1987)
8. J Coetzer and M J Notte, U S Patent 4592969 (1986)
9. R J Bones, D A Teagle, S D brooker, F L Cullen, Abstract No. 158, Extended Abstracts, 87(2), Electrochem Soc Fall Meeting, (1987) 230