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SODIUM SULPHUR BATTERY

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Sodium sulphur battery, being one of the most promising high energy density systems, is a potential candidate for the electric vehicle and utility load levelling. As a part of developmental programme, 5 and 20 Ah sodium sulphur cells have been tested to study their performance characteristics. Cell design, glass sealing before final assembly of the cell, corrosion resistance coating to the sulphur electrode container, freeze-thaw reliability etc. are discussed.

Key words: Sodium sulphur battery, thermo compression sealing, sulphur electrode, high energy density battery

INTRODUCTION

Sodium sulphur battery, being one of the promising high energy density systems, is a potential candidate for electric vehicle propulsion and utility load levelling. In this battery, sodium acts as the negative electrode and sulphur as the positive electrode and both these electrodes are liquids at the operating temperature, 623K. The electrodes are separated by beta alumina separator which also acts as a conducting medium for transport of sodium ions. As a part of the developmental programme, 5 and 20 Ah sodium-sulphur cells have been tested to study their performance characteristics. Cell design, glass sealing before final assembly of the cell, corrosion resistance coating to the sulphur electrode container, freeze-thaw reliability, etc are discussed in the present communication.

RESULTS AND DISCUSSION

Cell reactions

The overall cell reaction in a sodium sulphur cell can be written as [1]

$$2\,Na + x\,S \rightleftharpoons Na_2\,S_x \qquad \ldots (1)$$

A potential of 2.078 V is observed at the operating temperature of the battery, with the cell fully charged. During discharge, sodium ion transport to sulphur compartment takes place and sodium sulphide is formed. During charge, sodium ion from polysulphide is again transported through beta alumina to sodium compartment.

Cell design

Cell design for 5 Ah cell was discussed earlier [2]. For a 20 Ah cell with beta alumina tube of 50 mm dia, (obtained from National Physical Laboratory, New Delhi), the cell has been designed according to the equation [3]

$$V = \pi\, D^2\, (L + L_t)/4 \qquad \ldots (2)$$

where V = Cell volume, D = cell diameter equal to $(d + 2t_s)$ ('d' corresponds to diameter of the beta tube; 't_s' is the sulphur electrode thickness), L = length of the cell case, L_t = length of the cell terminals The cell thus designed is shown in Fig. 1.

Cell assembly

Beta alumina tubes (50 mm dia) were initially tested for helium leak rate at BHEL, Trichy, India as well as with purified moisture free argon leak rate at CECRI, Karaikudi. Some of the tubes were found to be leaky at the glass sealing portion. These tubes are resealed with sealing glass powder at 1473K for half an hour in Keramax furnace. The tubes thus sealed were tested for leak rate with moisture free pure argon. Tubes which had withstood the above tests were assembled in the cell with suitable washers.

Fig. 1: 20 Ah sodium sulphur cells

Sodium filling

High purity nuclear grade sodium was filled (at IGCAR, Kalpakkam, India) in a glove box inside which oxygen content was kept at a minimum (less than 10 ppm).

Development of thermocompression seal

Development of ceramic to metal sealing by diffusion bonding [4] is essential as it will provide a good hermetic seal in the final cell assembly while resulting in a light weight cell. This was tried (at IGCAR, Kalpakkam) in a specially constructed vacuum chamber where predetermined load is applied to the parts to be bonded (metal to ceramic) at the desired temperature. This was developed and bonding strength was tested. More experiments are needed to get a good seal with the required bond strength between metal and ceramic. Parallel studies have been carried out at CECRI, based on the above results obtained and the facility to do the job has been created. As a part of the programme, thermocompression bonding of ceramic to metal by hot isostatic pressing is under development (at DMRL, Hyderabad.) Since the technology of thermocompression sealing is not available right now, mechanical sealing has been adopted in the present study.

Corrosion resistance coating development

The mild steel casing which also acts, as the current collector and cathode container, was coated with chromium from acid chromate bath to a thickness of 60–80 μm. Chromium plated cell was heated to 473K for 6 h and to 1273K for 1 h in an inert atmosphere to enable diffusion process. Diffused chromium acts as a protective layer towards corrosion of molten polysulphides during the operation of the cell [5].

Sulphur electrode

Based on the results from 5 Ah cell [2] and other reports [6,7], dual mat sulphur electrode design was preferred and sulphur electrodes are mostly preformed in a specially designed die, as reported earlier [2]. The resistance of the sulphur electrode determined at room temperature was 250 to 500 mohm.cm. As a part of characterisation of the sulphur electrodes, transient measurements were made using a simple glass cell set up where the electrolyte was the molten polysulphide (prepared by refluxing a mixture of molten sodium and sulphur slurry in a boiling toluene and xylene mixture for 4 h, washed with hot toluene, vehicle removed by vacuum distillation at 393 K for 16 h and then melted and stored under vacuum in a sealed glass vessel.). RVC 4000 felt impregnated with sulphur in the form of a cylindrical rod and with Mo wire as contact lead acted as working electrode (which formed an exposed cross sectional area of 0.2 cm^2). Molybdenum electrodes were used as counter as well as reference electrodes. A galvanostatic pulse was applied between working and counter electrodes. The overvoltage, η, was recorded with time. From the response η vs t, the sulphur electrode resistance was calculated and the values are in the range, 0.4 to 2 ohm.cm. which is in agreement with the reported values [8]

Cycle life and freeze-thaw reliability

Earlier cells showed limited cycle life of less than 20. Two cells had been stopped due to loss of capacity and increase in cell resistance with number of cycles. This may be due to the deposition of elemental sulphur on the beta alumina tube during charging in spite of providing a high resistive layer at the interface. The layer is formed by the decomposition of aluminium sulphate [9] and aluminium nitrate [10]. In aluminium nitrate decomposition, it is stated [9] that resistance of the sulphur electrode would progressively increase. Although it is claimed [9], that resistance does not increase with number of cycles (in the aluminium sulphate decomposition), it is not so in actual practice. This may be due to the presence of sulphate ions resulting from incomplete decomposition of aluminium sulphate at the reported temperature. However, by using the nonresistance carbon paper obtained from Materials International, USA, this problem has been overcome and recharging could be accomplished without polarisation. In the other cases of tests, increase in cycle life could not be achieved due to freeze-thaw reliability, in spite of low internal resistance of the cells operated (30 to 70 mohms). In these cells, the resistance of sulphur electrode varies from 10 to 30 mohms as calculated from transient studies of sulphur electrode in sodium polysulphides. Resistance contributed by beta alumina is 16 to 30 mohms as calculated from the resistivity values provided by NPL, New Delhi (8 to 15 ohm.cm for a wall thickness of 2 mm of 50 mm dia for the beta alumina tubes). During freeze-thaw cycle tests, beta alumina tubes yield and due to exothermic reaction of sodium with sulphur, the stainless steel mesh inside beta alumina as well as the negative electrode terminal gets deformed. This may be due to poor mechanical strength of beta alumina tubes. However, steps have been taken to modify the sulphur electrode in order to get better freeze-thaw reliability.

CONCLUSION

A 20 Ah cell has been designed and its performance characteristic studied. Sulphur electrode has been designed and resistance values obtained are in agreement with the reported values. Steps are being taken to get better freeze-thaw reliability and in turn better cycle life.

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