ACCELERATED LIFE TESTING OF SODIUM–SULFUR CELLS

GERHARD LEHNERT

Brown, Boveri & Cie, AG Abt. EA, Eppelheimer Str. 82, D-6900 Heidelberg (F.R.G.)

Introduction

Currently, there is great interest in many countries in the development of the sodium–sulfur battery for Electric Vehicle (E.V.) and load leveling applications [1]. One of the most critical steps in such developments is the achievement of a sufficient life and also the experimental verification of this value. For an E.V. battery the goal for life is greater than 1000 cycles, therefore practical application testing would last several years. For this reason the need for accelerated life testing of batteries for this application is out of the question. For some battery systems [2] — especially for lead–acid batteries [3] — some accelerated testing procedures have been developed, but these depend on the special degradation mechanisms of the investigated batteries and cannot be generalized.

The aim of this work was to investigate the behavior of sodium–sulfur (Na/S) cells under accelerated test conditions, and from this to select procedures that result in high time acceleration without changing the dominant mechanisms of degradation.

Experimental

Statistically designed experimental methods [4] were used to reduce the required testing capacity and to simplify the analysis of significant effects. From preliminary tests the four factors, temperature, charge current, discharge current, and final charging voltage, were selected and put in two fractional factorial designs. The temperature was varied at 3 levels (standard 350 °C, 300 °C, and 400 °C); the charge/discharge constant current was partly increased by a factor of three compared with the former current (8 A/16 A corresponding to a charging/discharging time of about 4/2 h). The final charging voltage was 0.5 or 1 V higher than the respective voltage plateau; the end of discharge voltage was, in each case, fixed at the fully discharged state (deep discharge to melt composition Na_2S_3). The cycling was carried out continuously, with a pause of 6 min only between charge and discharge.

In total, twelve different experiments resulted from the factorial design; each experiment was undertaken with 3 - 5 single cells. The cells were cycled to failure by an automatic cycling apparatus controlled by a minicomputer.

Results and discussion

The evaluation was done with the mean values from the 3 to 5 cells of each experiment using variance analysis.

The capacity decline was strongly influenced by the temperature. At 400 °C the capacity decline was increased by a factor of 2 - 8 by comparison with the value in the temperature range 300 - 350 °C.

The influence of the discharge current is obviously also affected by the increased temperature (the cells were not cooled during cycling). *Post-mortem* investigations detected cell casing corrosion as the cause of the high capacity decline at 400 °C.

The resistance of the cells was stable for all experiments and for the whole duration of cycling.

The life of the cells was limited by the rupture of the β-Al_2O_3 electrolyte (no capacity limit was defined). Temperature had the most influence on the electrolyte failure. The low life of the cells operated at the highest temperature, 400 °C, may be correlated with high corrosion in this case, *i.e.*, high cell degradation could lead to accelerated electrolyte damage.

During time of operation, a reduction in cycles due to capacity decline occurs. To eliminate this, the totally transported charge in one direction per electrolyte area is used to characterize the life. The dependence of this life value on temperature does not correlate well with linear and Arrhenius models [5]. From this we may suppose that at a temperature of 400 °C the failure mechanism changed.

In the temperature range from 300 to 350 °C, the charging and discharging current factors also showed effects on life. By increasing the charging current, life was reduced, but at the higher discharge current life was improved.

Life reduction in charging is in agreement with electrolyte degradation models which predict that charging — especially with high current density — is critical [6, 7]. There is no theory, however, for improved life at increased discharge current (a time dependent factor of electrolyte degradation could be an explanation).

The fourth factor (final charging voltage) of the factorial design showed no effect on life.

The resulting life as a function of testing duration indicates a shortening of testing time under some test conditions. The goal for an optimized acceleration procedure is to obtain the greatest acceleration factor and, simultaneously, a clear correlation with degradation and life under standard conditions. With this criterion, we see that in the temperature range 300 - 350 °C the increase in current by a factor of three is the best acceleration procedure. At 400 °C we obtain even shorter testing times, but from the extreme change in degradation and life data we must assume that the failure mechanism has changed.

With the optimized accelerated testing procedure, an acceleration factor greater than 4 by comparison with standard cycling (3 cycles per day)

results. For actual application with a maximum of one cycle per day, a total acceleration factor of greater than 10 is achievable.

Conclusion

The operation of Na–S cells at elevated temperature results in an increase in the capacity degradation of the cells and a reduction in the life of the β-alumina electrolyte. Charging is more critical in respect of electrolyte failure than is discharging. An accelerated cycling procedure for Na–S cells, with an acceleration factor greater than 10, was found, *i.e.*, a life of 1000 cycles can be demonstrated within 100 days. The results of the experiments with the Na–S single cells will provide information concerning the life potential of a complete Na–S battery. Experimental verification of battery life is still to be demonstrated, but from the results presented here we may assume that similar accelerated cycling procedures are applicable to the complete Na–S battery.

References

1 *Proc. DOE/EPRI Beta (Sodium–Sulphur) Battery Workshop V, Washington, D.C., Oct. 1983, EPRI Spec. Rep. EM-3631-SR.*
2 J. E. Clifford and R. E. Thomas, *Batelle Columbus Lab./Sandia Contractor Rep. SAND 82-7049*, April, 1982.
3 N. J. Maskalick, *J. Electrochem. Soc., 122* (1975) 19.
4 S. L. Basin and B. Spindler, *EPRI Tech. Rep. EM-1346*, 1980.
5 W. Nelson, *IEEE Trans. Electr. Insul., EI-9*, (1974) 12.
6 A. V. Virkar and L. Viswanathan, *J. Mater. Sci., 18* (1983) 1202.
7 L. C. De Jonghe, *Lawrence Berkeley Lab. Rep. LBL-16716*, 1983.