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A safe, fast-charge, two-volt lithium/polymer cathode 'AA'-size cell with a greater than 250 Wh kg^{-1} energy density

John Broadhead *, Terje Skotheim

Moltech Corporation, 9000 Rita Road, Bldg. 061, Tucson, AZ 85747, USA

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Abstract

Research and development of organo-sulfur polymer composite cathodes has produced a family of materials which are electroactive and rechargeable in non-aqueous systems. This paper describes the latest improvements in the performance of AA-size cells and indicates directions to be taken for further development. Applications-oriented performance characteristics (including high-rate charge and GSM pulse discharge) of AA-size cells are described. Initial Regulatory Agency abuse tests are outlined.

Keywords: Lithium secondary batteries; Organosulfur cathodes

1. Introduction

Beginning in 1988, research and development has led to identification of a new, safe high-energy density lithium battery. This is a new area of technology and has been described at recent symposia [1–6]. The battery employs a lithium–organo-sulfur composite electrochemical system that exhibits good cycle life and is safe for consumer applications. The synthesis and evaluation of one of these organo-sulfur polymers is outlined in a recent publication [5]. More recent tests have been carried out in AA-size (14 500) hardware. The cell demonstrates a major improvement in gravimetric energy density over lithium-ion cells and shows significant improvement in volumetric energy density over this system. The cell also demonstrates safety in both UL and JSBA abuse tests.

2. Preparation and performance

Synthesis of one of the organo-sulfur compounds has been reported previously [7,8]. This is (poly)carbon disulfide, PCS, which is obtained by the polymerization of carbon disulfide.

This material is capable of reversible multi-electron reduction–oxidation, providing specific energies of about 1000 Wh kg^{-1} of cathode active material. Modification of the synthesis conditions resulted in appearance of new versions of PCS with different properties. Three different syntheses are described:

(i) PCS I materials are obtained when sodium metal is dissolved in dimethyl sulfoxide in an argon atmosphere, followed by dropwise addition of carbon disulfide;

(ii) PCS II materials are obtained by an inverted synthesis, when dimethyl sulfoxide is added to a sodium suspension in boiling carbon disulfide;

(iii) PCS III materials are obtained by inverted synthesis at increased temperature (135 instead of 50°C).

Physico-chemical analysis demonstrates that all forms of PCS are mixtures of at least three components, with ratios which are dependent on synthetic conditions and post-synthesis treatment. Polysulfide fragments and [1,2]-dithiolo-(4,3c)-1,2-dithiole-3,6-dithione (DTTT) derivatives are suggested to be the two main components. Fig. 1 shows some likely fractions formed in the reaction.

The electrochemical properties of PCS I and PCS II were studied. Figs. 2 and 3 show cyclic voltammetric traces of these systems with lithium as a reference potential and a DMSO-based electrolyte. Both show two quasi-reversible redox peaks consistent with a two-step redox process. The observed peak shape, peak potentials and scan-rate dependence are similar to that of the reduction of elemental sulfur [7,8]. The peak-to-peak separation of about 500 mV on the first step, and less than 250 mV on the second, is lower than that of disulfide-bonded compounds, where it is close to 1 V [9,10]. Thus, charge transfer rates for PCS polymers should be significantly higher, opening the possibility of high-rate

* Corresponding author.

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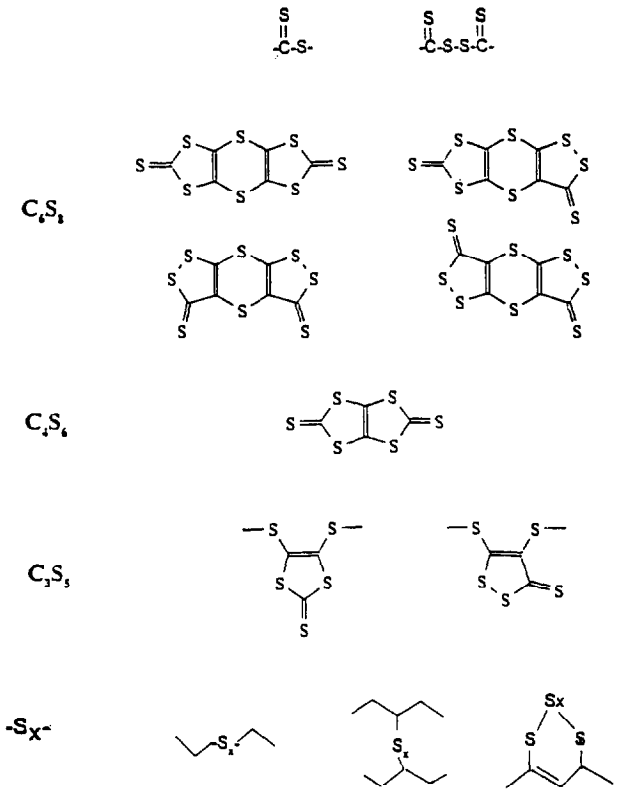

Fig. 1. Possible fragments of the PCS structure.

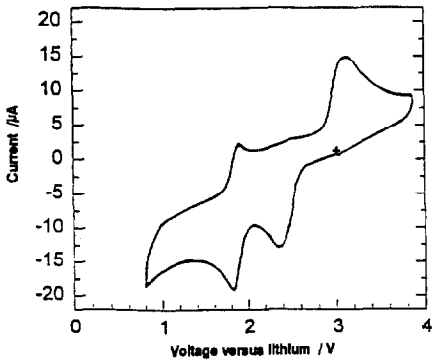

Fig. 2. Cyclic voltammogram of PCS 1 at a glassy carbon electrode in DMSO/Bu_4NBF_4 electrolyte. Scan rate was 200 mV s^{-1}.

applications. To check performance, an experimental wound cell was fabricated with PCS II, a lithium electrode and a DMSO-based electrolyte. Fig. 4 shows the initial discharge curve of this cathode material. It demonstrated about 1000 mAh g^{-1} of cathode active material but showed a fast fading of capacity. PCS I, though lower in capacity, demonstrated longer cycle life. Fig. 5 shows the cycle life of this material. Based on these initial successes, a search for improved, higher sulfur polymers was initiated.

Several new organo-sulfur cathode materials have been synthesized and we report here performance results from some of those new materials. The Li–organo-sulfur composite system is particularly suited to high-rate applications, such as the digital cellular pulse regimes (GSM and D-AMPS phones). Fig. 6 shows a discharge curve under GSM pulse conditions. Fig. 7 shows the cycle life of this cell.

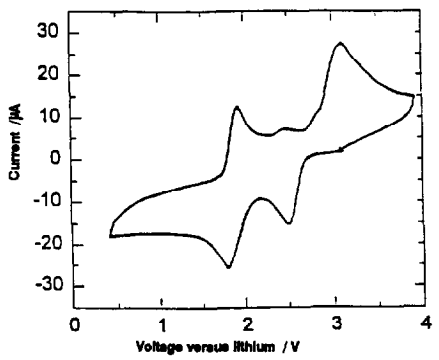

Fig. 3. Cyclic voltammogram of PCS 11 at a glassy carbon electrode in DMSO/Bu_4NBF_4 electrolyte. Scan rate was 200 mV s^{-1}.

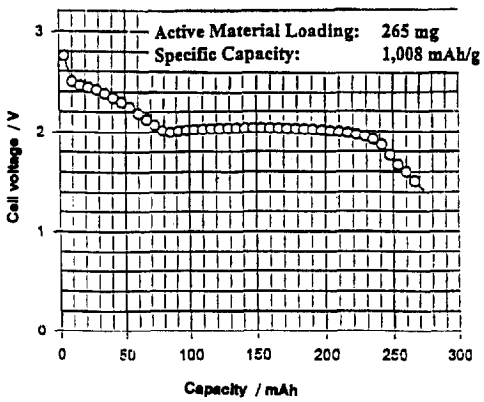

Fig. 4. First discharge of an Li/PCS 11 experimental wound cell at 100 mA.

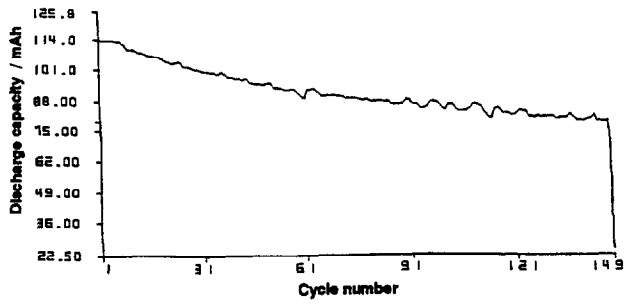

Fig. 5. Discharge capacity vs. cycle number for the cell with PCS 1 cathode material cycled at a charge/discharge current of 100 mA.

The specific capacity of the positive electrode active material is considerably higher than that of any metal oxide system, and the bulk density is low. These characteristics allow the AA-size cell to attain 260 Wh dm^3 and 180 Wh kg^{-1}. Future improvements should increase the AA-size cell performance to 400 Wh dm^3 and 400 Wh kg^{-1}. Already initial data are indicating increases in capacity and reduction in weight that demonstrate that specific energies in excess of 230 Wh kg^{-1} are close at hand.

The proprietary positive electrode and the electrolyte also impart significant advantages to the system. Dendritic growth on the lithium anode during charge has been suppressed, enhancing safety and cycle life, and because there is a shuttle effect allowing excess current to pass it is possible to equalize cells in a string.

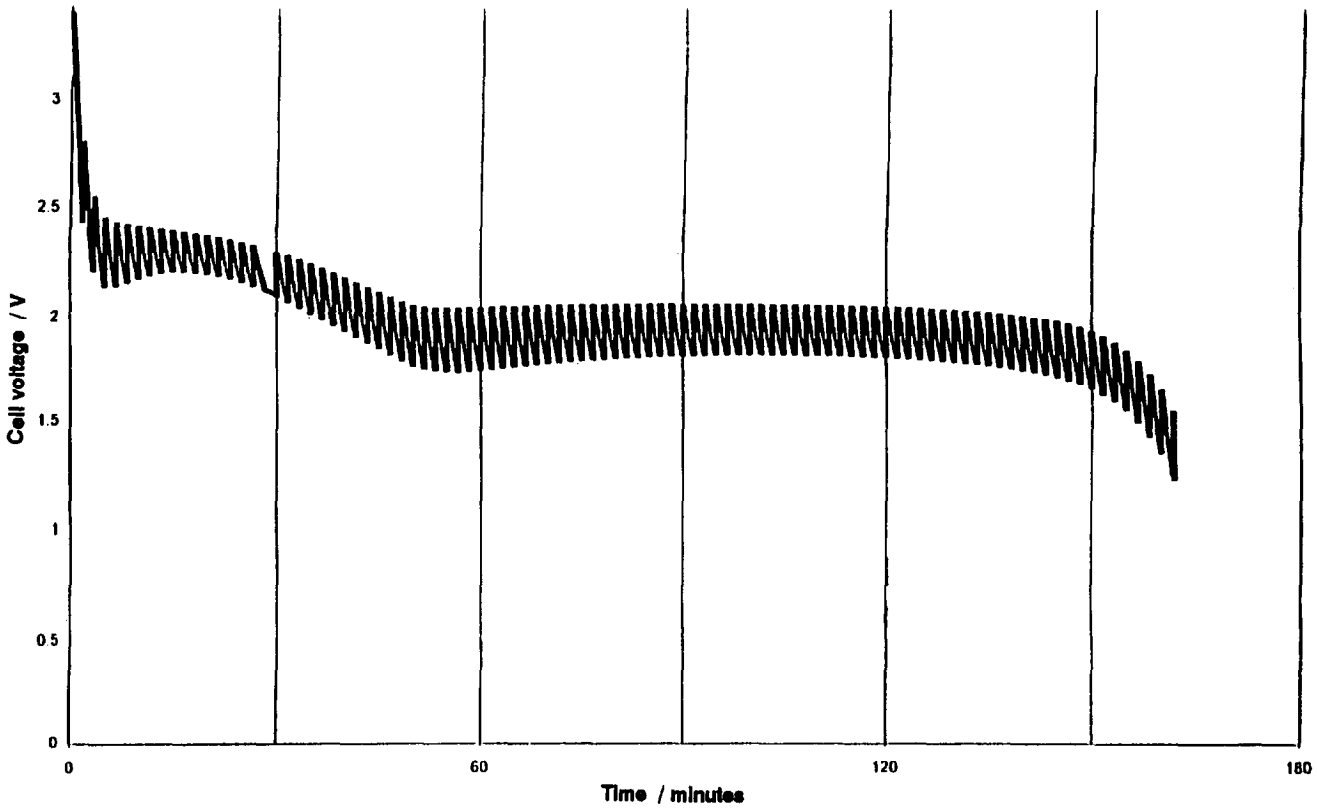

Fig. 6. AA-size cell discharged under GSM pulse conditions: 1.5 A, 0.6 ms; 0.1 A, 4.4 ms.

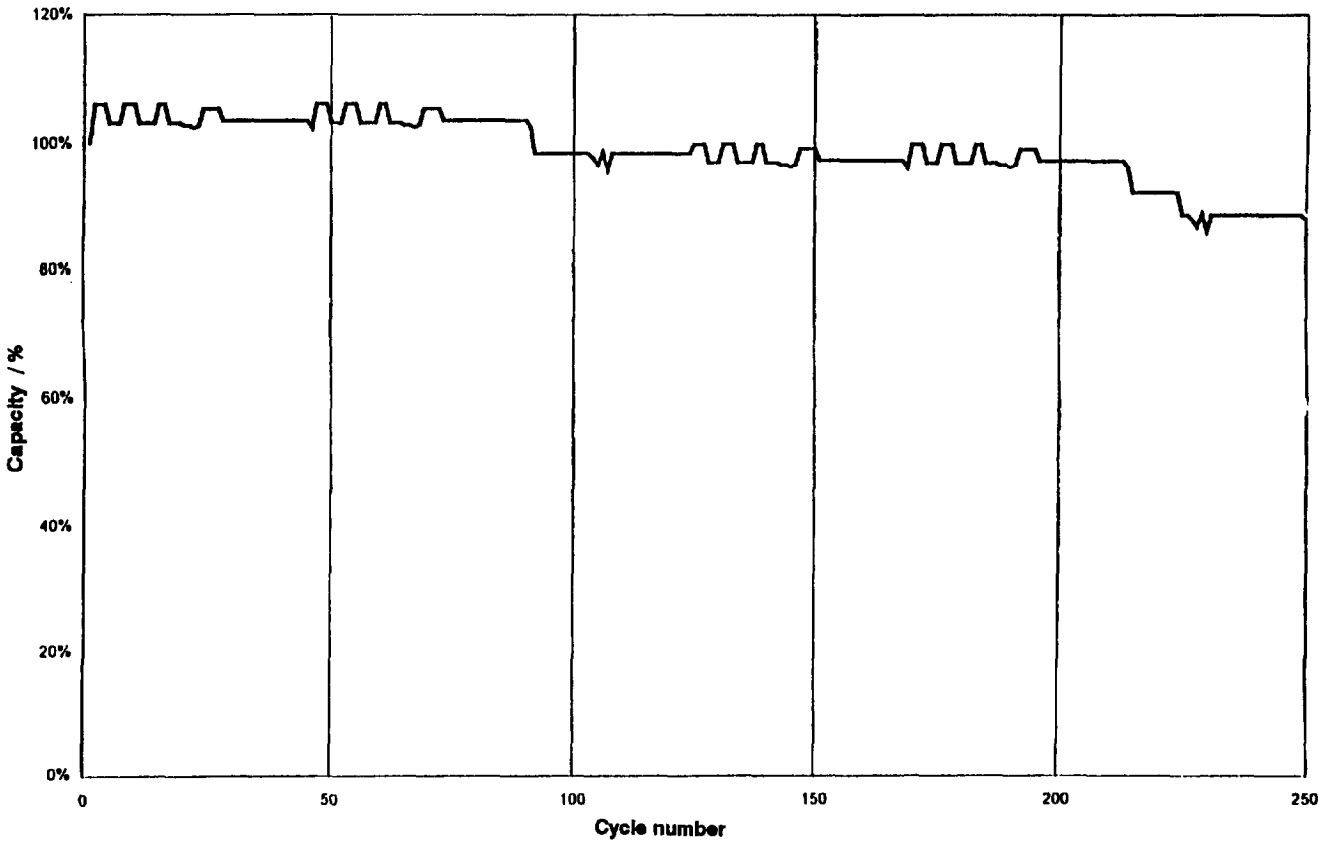

Fig. 7. Cycle life of AA-size cell under GSM pulse conditions.

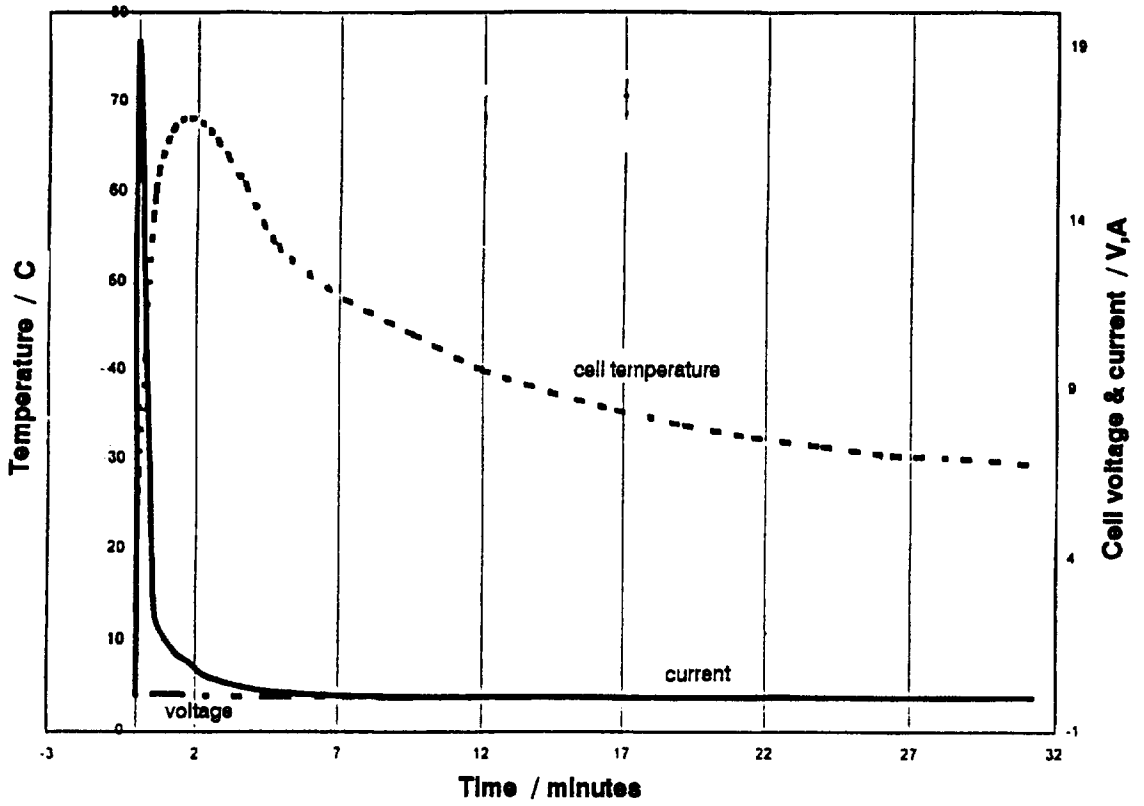

Fig. 8. AA-size cell: safety performance under UL short-circuit conditions.

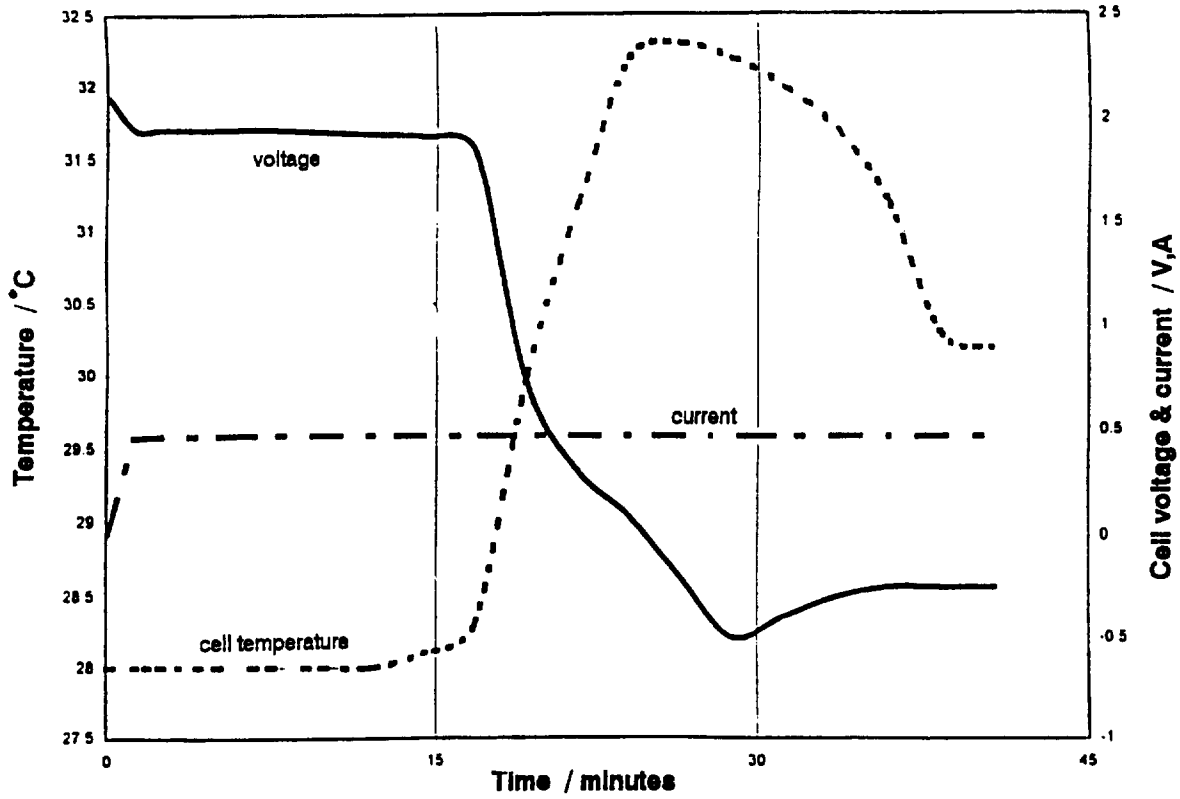

Fig. 9. AA-size cell in JSBA forced discharge test at 450 mA.

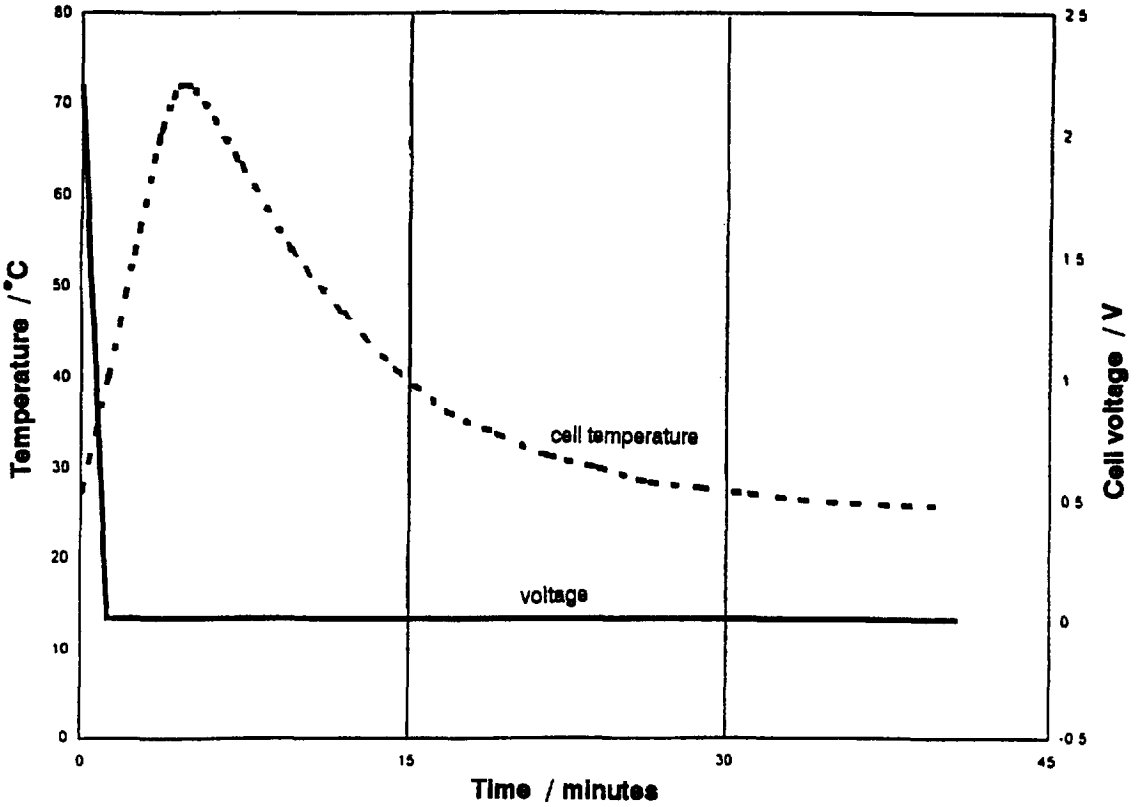

Fig. 10. AA-size cell in UL crush test.

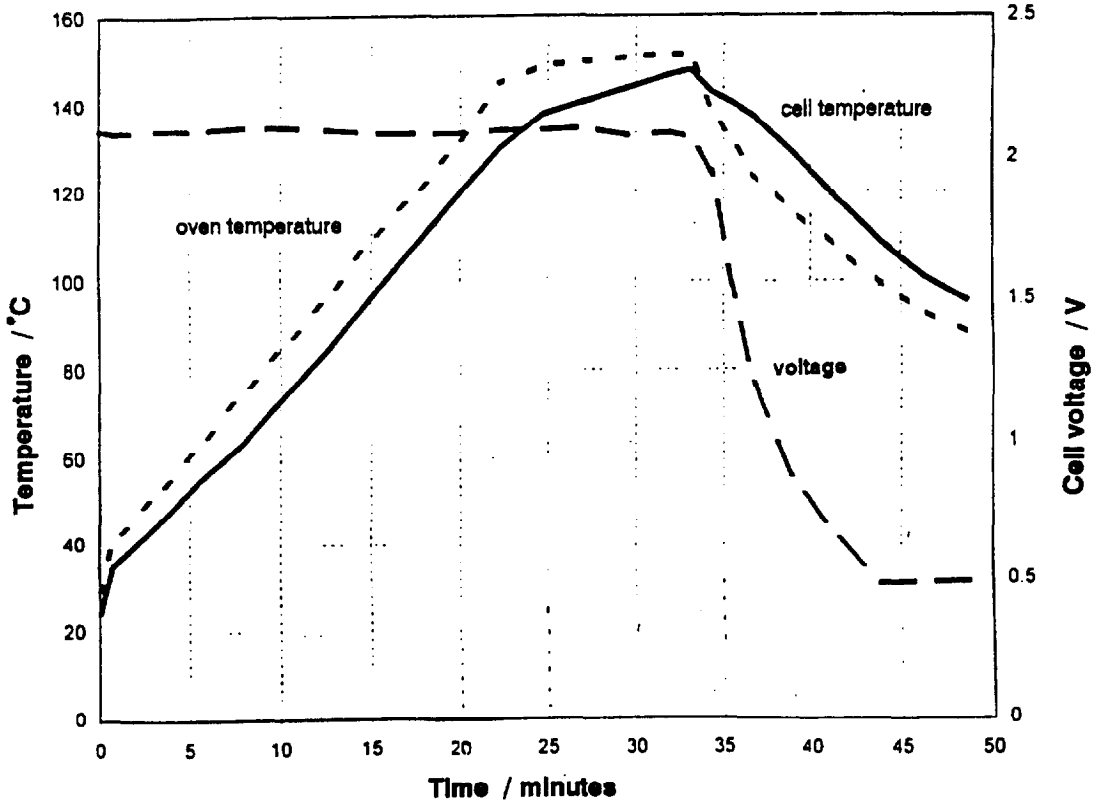

Fig. 11. AA-size cell in UL heating test.

3. Safety

Due to the previously mentioned electrochemical behavior, the cell has intrinsic safety characteristics 'built-into' the chemistry. The formation of dendrites is suppressed and there is an inherent over-charge mechanism and an excellent tolerance to over-discharge.

The AA-size cell has successfully undergone the range of UL and JSBA abuse tests. Figs. 8–11 show examples of some of these tests.

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