


# Image Cover Sheet

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**TITLE**  
DECOMPOSITION OF ACETONITRILE IN DISCHARGED Li/SO<sub>2</sub> CELLS

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DECOMPOSITION OF ACETONITRILE IN DISCHARGED  
Li/SO<sub>2</sub> CELLS

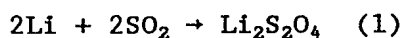
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The Li/SO<sub>2</sub> battery system exhibits a number of desirable properties (high energy density, excellent low temperature performance, long shelf life) which make it well-suited to many military applications.

The cell chemistry is based on the oxidation of metallic lithium and the reduction of sulphur dioxide to produce lithium dithionite, the generally accepted main reaction product.



The electrolyte used is a mixture of LiBr, SO<sub>2</sub>, and acetonitrile (ACN). Earlier studies on Li/SO<sub>2</sub> reserve cells<sup>1</sup> indicated that the electrolyte was not stable for prolonged periods and that decomposition was significant at elevated temperatures. In addition, our own experiments<sup>2</sup> have confirmed that metallic lithium and ACN are not stable in direct contact. The reaction is analogous to the known reaction between metallic sodium and ACN<sup>3</sup>:



Many other compounds are also formed here<sup>4</sup>, including higher nitriles (di/triacetonitrile etc.).

The Li/SO<sub>2</sub> cell is viable due to the formation of a passivating layer on the Li anode, formed in the presence of SO<sub>2</sub>.

Previous work in our laboratory<sup>5</sup> showed that ACN decomposition occurred in both balanced (Li/SO<sub>2</sub> ≈ 1) and lithium-rich (Li/SO<sub>2</sub> > 1) cell configurations. Cyanide ion was also detected in cell extracts. The large amounts of ACN which could not be recovered from discharged cells upon post-mortem, combined with our cyanide results, raised questions as to the reliability of the analytical methods in view of the complexity of the sample matrix.

The present investigation was undertaken in an effort to develop sensitive and selective methods for determining free cyanide and other ACN decomposition products in Li/SO<sub>2</sub> cells, to determine the conditions leading to ACN decomposition, and to evaluate environmental hazards associated with their disposal.

### Analytical Techniques

Ion chromatographic and liquid chromatographic techniques were developed which led to the ability to determine cyanide, thiocyanate, and metal-cyanide complexes. Gas chromatographic techniques were developed to analyze cells for diacetonitrile, triacetonitrile, and volatile hydrocarbons. Other analytical techniques were utilized in an effort to better characterize other ACN decomposition products.

### Conditions Leading to ACN Decomposition

Commercial cells of differing coulombic balance were discharged under a variety of conditions. These cells were taken from in-house and external inventories and represented different manufacturers and ages. The study examined cells which were resistively discharged or force overdischarged under constant current conditions (individually or as multi-cell batteries) at various temperatures. A wide range of storage intervals after discharge (0-4 yrs+) and temperatures were also evaluated.

Of the balanced cells analyzed to date, those resistively discharged at  $-25^{\circ}\text{C}$  and stored for several years after discharge have shown no evidence of ACN decomposition (these cells also contained significant quantities of residual  $\text{Li}^{\circ}$  and  $\text{SO}_2$ ). Those subjected to an exhaustive resistive discharge at  $20^{\circ}\text{C}$  and then stored for several years have shown significant ACN decomposition (most of these cells to-date contained no significant residual  $\text{Li}^{\circ}$  or  $\text{SO}_2$ ).

Balanced cells resistively discharged at  $45^{\circ}\text{C}$  to varying end voltages then immediately opened have shown no signs of significant ACN decomposition. These cells contained varying amounts of residual  $\text{Li}^{\circ}$  and  $\text{SO}_2$  depending on the capacity withdrawn.

All balanced cells subjected to an exhaustive resistive discharge to-date at  $45^{\circ}\text{C}$  then stored have shown signs of ACN decomposition. At this point in the work, cells which were stored for 3-4 years after discharge have displayed the most significant degree of ACN decomposition (in one instance @ 80 % of the original ACN content decomposed). Previously undischarged cells which were greater than 4 years old and were then exhaustively discharged at  $45^{\circ}\text{C}$  also showed signs of ACN decomposition. From the results to-date, the extent of ACN decomposition appears to increase with storage duration after discharge and with temperature.

As expected, cyanide content has been highest in lithium-rich cells. Thiocyanate has been found in all types of cells. Iron and nickel cyanides have been found commonly, particularly in balanced cells where internal can and current collector corrosion is evident.

To facilitate data interpretation, investigations are being conducted using custom-made commercial cells where the  $\text{Li}/\text{SO}_2$  coulombic ratio is varied from 0.9 to 1.1.

Work is also ongoing to characterize other ACN decomposition products, which may be formed in the cells, in an effort to better understand the mechanisms involved. It is possible that other electrolyte components are involved in the decomposition of ACN in  $\text{Li}/\text{SO}_2$  cells.

### Acknowledgements

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