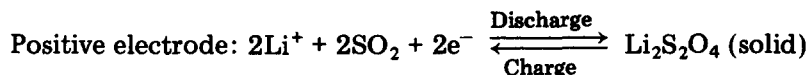
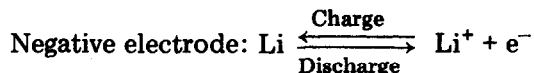


ALL-INORGANIC AMBIENT TEMPERATURE RECHARGEABLE LITHIUM BATTERY

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The objective is to establish the technical feasibility of a sulfur dioxide-based all-inorganic ambient temperature rechargeable lithium battery with an initial cycle life goal of 100 cycles at 80 percent depth of discharge.

Duracell, Inc., has developed an all-inorganic Li/SO₂ rechargeable battery system that operates at ambient temperature and is capable of delivering an energy density of 330 W h/kg. The system consists of a lithium negative electrode and a porous carbon/SO₂ positive electrode. Liquid SO₂ containing an inorganic salt such as Li₂B₁₀Cl₁₀ is employed as the electrolyte and the liquid depolarizer. The cell reactions are as follows:



During the discharge cycle, Li₂S₂O₄, an insoluble solid, is formed within the porous carbon electrode. The solid Li₂S₂O₄ is converted back to liquid SO₂ and Li⁺ ions during the recharge cycle. The reversibility of the lithium electrode and the carbon/SO₂ electrode in the inorganic electrolyte has been established.

A joint effort with the Department of Energy under a 50:50 cost shared program was initiated earlier under Contract No. DE-ACO1-80ER-10191. We have achieved a cycle life of 50 to 130 cycles at 10 to 20 percent depth of discharge in hermetic D cells. Exploration of a low cost alternative to the expensive Li₂B₁₀Cl₁₀ salt has also been carried out. A follow-on 3-yr program for further development of the inorganic lithium rechargeable system has been started recently. The ultimate goal is to improve the performance of the system to obtain a cycle life of 500 to 800 cycles at 80 percent to 100 percent depth of discharge. The emphasis in the first year of the follow-on 3-yr program is placed on the improvement of the experimental flat electrode cells to show good cyclability at 80 to 100 percent depth of discharge. The initial goal is to achieve a cycle life of 100 cycles at 80 percent depth of discharge.

Previous cell evaluation results indicated that the cycle life of the Li/SO₂ system was primarily limited by the degradation of the porous carbon electrode. The failure-mode analysis of the carbon electrodes of spirally wound D cells was carried out further by examining the cathodes of fully discharged and fully charged cells. After complete discharge, the carbon

electrode became very hard and brittle due to saturation with the insoluble reaction product, $\text{Li}_2\text{S}_2\text{O}_4$. After recharge, the carbon electrode returned to its original flexible condition. The formation of the solid $\text{Li}_2\text{S}_2\text{O}_4$ within the pores generates large internal stresses in the carbon electrode matrix and breaks the electrical contact of some of the carbon particles. This may cause irreversible damage. Repeated change of the mechanical structure of the carbon electrode during discharge and charge causes the degradation of the electrode performance. A variety of approaches were attempted to improve the mechanical integrity of the porous carbon cathode with very limited success. On shallow cycling (10 to 20 percent depth of discharge), the carbon cathodes do not deteriorate as rapidly, and cycle life in excess of 100 cycles has been achieved. However, on deep cycling (80 to 100 percent depth of discharge), the carbon cathode deteriorates rapidly within 20 to 40 cycles.

This cathode problem was circumvented by using a new proprietary positive electrode material to be referred to as CX1, which was found to be compatible with the sulfur dioxide-based inorganic electrolyte. Efforts were concentrated on the evaluation of this active positive electrode material during this year. The liquid SO_2 in the Li/CX1 system acts as a solvent only for the electrolyte; it is not involved in the cell reaction during charge and discharge. An experimental cell demonstrated 400 deep cycles at 1-mA/cm^2 charge rate and 2-mA/cm^2 discharge rate between the cutoff voltages of 2.6 V and 4.05 V before failure due to the malfunctioning of the cycling system. The CX1 electrode can deliver 50 percent of its theoretical capacity to the cutoff voltage of 2.6 V. Discharging the cell to a voltage lower than 2.6 V was found to have an adverse effect on the cycle life. Increasing the charge rate to higher than 1 mA/cm^2 also decreases the cycle life. Methods to improve the rate capability and the capacity utilization of the CX1 electrode are being actively explored. The theoretical energy density of this system is slightly higher than that of the Li/ SO_2 system.

The electrolyte salt, $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, in liquid SO_2 is extremely expensive (\$2300/lb), and therefore, a major effort for the exploration of new lower cost electrolytes for the Li/ SO_2 rechargeable battery was undertaken. As a result of this effort, a new lower cost proprietary electrolyte salt (to be referred to as EX1) that provided highly conducting solutions in liquid SO_2 was discovered. This electrolyte was evaluated in the Li/ SO_2 spirally wound D cells. The cells exhibited comparable cycling performance at shallow discharge and somewhat better performance on deep discharge compared to the cells with $\text{Li}_2\text{B}_{10}\text{Cl}_{10}\text{-SO}_2$ electrolyte.

Another low cost, highly conductive electrolyte ($1 \times 10^{-1}\text{ ohm}^{-1}\text{ cm}^{-1}$), was discovered and referred to as EX2. This new electrolyte works very well with the solid positive materials such as CX1. Unfortunately, it is incompatible with the carbon electrode of the Li/ SO_2 system. Electrochemical study of the EX1 and EX2 electrolytes indicates that both are stable within the operating voltage range of the Li/ SO_2 or Li/CX1 system.

Studies of the lithium cycling life in various inorganic electrolytes are in progress. Experimental cells with limited lithium electrode capacity were

made for evaluation at various rates and depths of discharge. Both the carbon electrode and the CX1 electrode were used as the counter electrode for this study. Preliminary test results show that the lithium electrode in the EX1 electrolyte has a cycling efficiency of 85 to 87 percent operating with the carbon counter electrode and a better efficiency of about 92 to 94 percent operating with the CX1 counter electrode. The current density of 0.5 to 2 mA/cm² had no significant effect on the cycling efficiency. The cycling efficiency of lithium in the EX2 electrolyte is estimated to be higher than 97 percent.

The development of an all-inorganic, ambient temperature, lithium solid cathode system using the low cost electrolyte will continue to be emphasized during the coming quarters.

The objectives for 1983 are to characterize CX1 cathode and Li anode cycling in the EX2 electrolyte and to establish the performance capability and identify the problem areas using experimental cells.

Recent publications

- 1 W. Bowden, Electrochemical oxidation of polyhedral boron halide anion, *J. Electrochem. Soc.*, 129 (1982) 1249 - 1252.

SULFOLANES AS ELECTROLYTE SOLVENTS FOR RECHARGEABLE LITHIUM BATTERIES

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The purpose of this research is to investigate the possible use of sulfolanes in rechargeable lithium batteries. The critical parameters are the conductivity of sulfolane electrolytes, the stability of these electrolytes, and the ability of the electrolytes to cycle lithium. Tests will be conducted on pure sulfolane electrolytes and on sulfolane blends with ethers.

To date, efforts in the program have been concentrated on the purification of sulfolane (S). In addition, the stability of S to Li (and Na/K) and the electrochemical limits of electrolyte solutions have been investigated. Conductivities of electrolyte solutions in S and S-ether mixtures have been surveyed. A test cell for half-cell Li cycling was developed, and initial cycling experiments were performed.

Sulfolane has commonly been selected for use as a solvent because of its resistance to oxidation. Many purification schemes are tailored for this application. The goal is to develop a purification scheme for the removal of