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INITIAL STUDY OF AN AMBIENT TEMPERATURE RECHARGEABLE LITHIUM-SULFUR DIOXIDE **BATTERY** 

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INITIAL STUDY OF AN AMBIENT TEMPERATURE RECHARGEABLE LITHIUM-SULFUR DIOXIDE BATTERY

William Bowden and A.N. Dey

June 1981

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Initial Study of an Ambient Temperature Rechargeable Lithium-Sulfur Dioxide Battery

#### Final Report on LBL Subcontract 4507410

June 1, 19BO to November 30, 19BO

Prepared for

LBL Project Manager: Philip N. Ross

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Work conducted at:

DURACELL INTERNATIONAL INC. Laboratory for Physical Science Northwest Industrial Park Burlington, Massachusetts 01B03

Principle Investigators:

William Bowden A. N. Dey

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#### Abstract

We made all-inorganic  $Li/SO<sub>2</sub>$  prototype rechargeable D cells with reference electrodes and demonstrated that  $SO<sub>2</sub>$  is deposited quantitatively in the catalytic carbon cathode as lithium dithionite  $\left(\rm L_{2}\rm S_{2}\rm O_{4}\right)$  during cell  $^{-}$ and the  $\frac{1}{2}$  discharge. We demonstrated that the  $\text{Li}_2\text{S}_2\text{O}_4$  is then quantitatively oxidized to SO<sub>2</sub> during the recharge portion of the cell cycle, according to the overall reaction

 $2Li + 2SO_2$   $L_1, S_2O_4$ 

We found that the electrolyte salt  $Li_2B_{10}Cl_{10}$  is oxidized in solution at slightly over the recharge potential of  $Li/SO<sub>2</sub>$  to give a one electron oxidation product. The oxidation product undergoes a further one electron oxidation to give a second product at potentials greater than those attained in cell recharge.

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#### I. Introduction

The Li/SO<sub>2</sub> .system is commercially available in a number of cell sizes as a primary battery system (1). Commercially available cells deliver an energy density of 150 W.hr/lb (330 Whr/Kg) or 8 W.hr/in<sup>3</sup> and power densities of 380 W/lb (836 W/Kg) or 21 W/in<sup>3</sup>. The Li/SO<sub>2</sub> primary system consists of a L1 fo11 anode, a porous carbon - PTFE catalytic current collector, and a catholyte consisting of acetonitrile,  $SO_2$  and LiBr supporting salt (1, 2). The postulated cell reaction  $[1]$  is based on qualitative tests  $(3)$ .

$$
2 \text{Li} + 2 \text{SO}_2 \longrightarrow \text{Li}_2\text{SO}_4 \qquad [1]
$$

The cell reaction product is lithium dithionite,  $\rm Li_2S_2O_4$ , an insoluble solid which precipitates in the porous carbon cathode, blocking further reduction of  $SO<sub>2</sub>$ . During storage and discharge the lithium anode is protected from chemical reaction with SO<sub>2</sub> by formation of a protective film of  $\rm L_{2}^{1}S_{2}O_{4}$ .

The revers ibility of the cell reactions is known (4). However, the cycle life is limited by the irreversible reaction of electrodeposited lithium with the acetonitrile organic cosolvent (5) forming lithium cyanide, methane and other more complex organic compounds (6) which could not be reoxidized back to soluble lithium salts. These lithium-solvent reactions lead to an irrevers ible los s of lithium. This problem can be eliminited by us ing the salt  $Li_2B_{10}Cl_{10}$  which is soluble in SO<sub>2</sub> and provides a highly conducting solution. In the Li/SO<sub>2</sub> system, comprised of a Li anode, porous carbon cathode and liquid  $SO_2$ cathode active material cum solvent with  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  electrolyte salt the only reaction occurring is the straightforward and reversible reaction  $[1]$ .

The salt  $Li_2B_{10}Cl_{10}$  is a member of the class of polyhedral borane anions and known to be extremely stable (7). There is some evidence to indicate that the  $B_{10}Cl_{10}^{2-}$  anion may be oxidized during charging to form a stable, soluble species. This oxidation of  $B_{10}Cl_{10}^{-2}$  is important in terms of providing overcharge protection of individual cells to balance the cells in a multicell battery. For example, in a lead-acid battery the electrolysis of solvent (water) provides this function.

Discharge:



Recharge:



The main goal for this six month program (LBL Contract #4507410) is to establish the validity or lack thereof of the above postulated reactions ..

The work statement for this program is as follows:

Investigate the properties of a rechargeable all inorganic electrolyte lithium battery cons isting of Li or Li-alloy negative electrode, porous carbon positive electrode and  $Li_2B_{10}Cl_{10}$  – SO<sub>2</sub> electrolyte.

Task I. Use hermetically sealed D cells with a Li reference electrode.

Task II. Identify the chemistry of the positive electrode reaction and verify that the discharge reaction products are rechargeable.

Task III. Report on the feasibility of this concept as a battery technology for use in electric vehicle or energy storage.

The results obtained during this contract are presented here.

#### II. Experimental

A. D Cell

To develop a hermetic D cell with reference electrode we selected the nickel plated cold rolled steel can used for  $Li/SO<sub>2</sub>$  cells that our company manufactures. This can incorporates both a filling eyelet and convoluted hermetic vent structure in the base as shown in Figure 1. The convoluted vent structure is designed to open under abusive conditions to render the cell safe. The identical vent or some modification may serve the same purpose with the rechargeable inorganic electrolyte cell. We fabricated a new top for the cell which incorporated two hermetic  $G/M$  seals instead of the usual one. We made both the G/M seals and cell tops in our laboratory as shown in Figure 2. As in a typical production cell, the porous carbon cathode is connected to the center post of a G/M seal by a welded tab while the lithium anode is connected to the can by a metal tab. The reference electrode was a Li foil which was wrapped with microporous' polypropylene separator, inserted into the electrode stack and welded to the centerpost of the second G/M seal. The anode and cathode are wound together in a jelly roll structure, insulated by layers of microporous polypropylene separator as shown in Figure 3. The complete electrode stack is inserted into the can, the electrode connections welded, and the cell top is attached by TIG welding. To fill, the cell is evacuated through the fill port and filled with  $SO_2$  electrolyte under pressure. The fill port is crimped shut and sealed by resistance welding to give a hermetically sealed cell.

#### B. Chemical Analysis

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Chemical analyses on the cells were performed by our analytical laboratory. The selected cells were punctured in a sealed bomb specially designed and built for the task, after which the volatile contents of the cell were removed under vacuum on a vacuum line we built for the task. The electrolyte was analyzed for  $SO_2$  by titration with NaOH in CH<sub>3</sub>CN to a bromcresol green endpoint. The spent cells were then taken into an argon filled glove box

and the top removed with a tubing cutter. The electrode stacks were removed and disassembled. The anodes were discarded after inspection while the cathodes were analyzed for dithionite (8). The dithionite was leached from the carbon cathodes in deoxygenated pH10 buffer and determined spectrophotometrically by bleaching a Cu (II) ammine complex. Lithium was determined by atomic absorption.

#### C. Cyclic Voltammetry

Cyclic voltammetry and coulometry were done with a PAR 173 Potentiostat and a PAR 175 Function Generator with cells of conventional design using a platinum wire or foil working and counter electrode with a silver wire or foil pseudoreference electrode. Normal pulse and differential pulse polarography (npp and dpp) were performed with a PAR 364 polarograph. Data collection was by conventional X-Y and stripchart recorders. Solvents were Burdick and Jackson "Distilled in Glass" acetonitrile and methylene chloride, used without further purification. The supporting electrolyte salt was tetrabutylammonium perchlorate  $(N(C_A H_Q)_A CIO_A)$ . (Southwestern Analytical, Electrometric Grade) kept at 70° C in a ventilated oven. Solutions were routinely degassed with Ar before use.

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#### III. Results and Discussion

A. D Cells

We prepared six D cells with reference electrodes to a standard design of electrode length, height and thickness and filled them with 0.25M.  $Li_2B_1_0Cl_{10}$  in  $SO_2$ , giving weights as shown in Table 1. The normally water white  $SO_2$  forms a yellow solution with  $Li_2B_1_0Cl_1_0$ . The presence of this yellow color has been cited as evidence for extensive anion solvation by the  $SO_2(9)$ . Cell 680-2 was rejected for low electrolyte weight and not used. The electrolyte salt used in this batch of electrolyte had  $0.31\%~\mathrm{H}_2\mathrm{O}$  by KF reagent. Later batches of  $\text{Li}_2\text{B}_1{}_{0}\text{Cl}_1{}_{0}$  were more carefully dried and contained around 250 ppm  $\text{H}_2\text{O}$ . One of these cells was completely discharged at O. SA at ambient temperature, giving 8.7 A.hr to a 2V cutoff. Two cells were selected for chemical analysis after discharge and recharge, respectively. One cell was discharged for 16 hours at 0.3A giving the voltage profile shown in Figure 4. The second cell was discharged for  $16$  hours at  $0.3A$  and then recharged at  $0.3A$  for  $16$  hours as shown in Figures 5 and 6 •. *A* relay was used to end the recharge at a cell voltage of *3.6V.* 

#### B. Chemical Analys is

The D cells were removed from the test area, punctured in the sealed bomb and the  $SO_2$  removed and collected on the vacuum line. Both cell  $SO_2$  extracts were dissolved in  $CH_3CN$  and titrated with aqueous base to a bromcresol green endpoint. Results of chemical analysis are shown in Table 2. The cell which had not been recharged contained 21.9 g SO<sub>2</sub> or 9.17 A.hr. The 9.17 A.hr  $SO_2$  remaining, plus the 4.8 A.hr used in the discharge gave 13.97 A.hr of  $SO_2$ , or 96% of the cathode active material originally found in the cell (680-6). The recharged cell contained 32.1 g SO<sub>2</sub> or 13.44 A.hr. This is a 96% recovery of active material from cell 680-4. The analysis of the discharged cell shows that  $SO_2$  is consumed in the cell discharge reaction through a one electron reduction of  $SO_2$  while the  $SO_2$  analysis of the recharged cell shows the quantitative regeneration of  $SO_2$  by oxidation of the discharge product.

The punctured cells were transferred in the sealed bomb to an argon filled glove box where they were opened with a tubing cutter and the electrode stacks removed. The discharged cell (680-6) had a rather stiff cathode which was somewhat brittle with a bright, flexible anode foil. The cathode was leached of dithionite in deaerated pH10 buffer and the leachate analyzed for  $\mathrm{s_2O_4}^{2-}$ . Cell 680-6 had 11.8 g or 0.092 eq.  $\mathrm{s_2O_4}^{2-}$ , which is 4.94 A. hr or 102% of the calculated depth of discharge. The specific analysis for lithium dithionite confirms  $Li_2S_2O_4$  as the  $SO_2$  discharge product and demonstrates the one electron reduction of  ${SO_2}$ .

The recharged cell (680-4) had a flexible cathode while the reactive anode surface tarnished even in the glove box atmosphere. There was some evidence of especially heavy Li deposition on electrode edges, but it was clear that both discharge and recharge had taken place throughout the length and height of the the electrode. The cathode of this cell contained  $\lt 10$  mg of  $\rm Li_2S_2O_4$ , indicating that  $100\%$  of the dithionite deposited in the cathode was oxidized to  $SO_2$  during the recharge.

The D cell is not a very satisfactory package for chemical analysis because of the difficulties in sampling and disassembling the hermetic package. The data we gained from these cells show, within the limits of the analyses, that Li/SO<sub>2</sub> cells show a quantitative reduction and reoxidation of SO<sub>2</sub> during discharge and recharge.

#### C. Cyclic Voltammetry

During early experiments evaluating the  $Li_2B_{1,0}Cl_{1,0}$  - SO<sub>2</sub> electrolyte, it was observed that cells showed a voltage plateau near 3.6V vs. Li. In there experiments intensely colored blue material was formed at the porous carbon at highly oxidizing potentials. We suspected that this blue material was an oxidation product of  $\mathtt{B_{10}Cl}_1^{-2-}$ , analogous to the oxidation products of  $\mathtt{B_gCl}_9^{-2-}$  $(10)$ . Since the reaction occurred at highly oxidizing potentials, we selected aceton itrile/N (bu)  ${_4}$ ClO<sub>4</sub> as a suitable electrolyte medium for this reaction.

A background voltammogram of the voltage region from  $0$  to  $+2V$ at 100 mv/sec for the  $CH_3CN/N(bu)_{4}ClO_4$  electrolyte is shown in Figure 7. A small amount of  $Li_2B_{1,0}Cl_{1,0}$  was then added, the solution again degassed with Ar, and the same voltage region swept again. As shown in Figure 8; a reversible wave near +1. 5V, or 3. 6V vs. Li was revealed. This wave can easily be assigned to the oxidation of  $B_{10}Cl_{10}^{2-}$  anion. A more sensitive cyclic voltammogram for 37.3 mg  $Li_2B_1{_0}Cl_{10}$  in 60 ml  $CH_3CN/N(bu)_4ClO_4$  (1.3 x  $10^{-3}$   $\underline{M}$ ) at 200 mV/sec is shown in Figure 9. In this voltammogram the reversible wave near 3. 6V from Li is clearly defined as well as a quasireversible wave near +1.1V which is probably due to an impurity in  $Li_2B_1_0Cl_{10}$ . The impurity is probably LiCl (11, 12). When the voltage limit on the scan was increased to the very high potentials of Z.5 - Z.8V vs Ag or 4.6 - 4. 9V vs Li, an irreversible wave was observed very near to background. There was no indication of any chemical reversibility in this'wave.

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To get a better idea of the stability of the oxidized form of  $Li_2B_1nCl_1n$ , we ran cyclic voltammograms at sweep rates from 50 to 500 mV/sec as shown in Figure 10. The result of these investigations are shown in Table 3. The  $\Delta E_{\rm p}$  values indicate a reversible one electron transfer slightly broadened by uncompensated solution resistance at higher sweep rates. From the increase in  $i_{pa}/i_{pc}$  from 0.86 to 0.95 with increase in V, there is some evidence for a comparatively slow reaction in solution. The oxidation of  $Li_2B_1_0Cl_{1,0}$  is diffusion controlled at a platinum electrode in acetonitrile as demonstrated by the linear plot of  $i_{pa}$  vs.  $\sqrt{V}$  shown in Figure 11.

We hoped that the subsequent chemical reaction observed in the oxidation of  $Li_2B_1$   $_0Cl_1$  was due to reaction with an impurity, either in the acetonitrile or supporting electrolyte salt. We decided to investigate the one electron stoichiometry of the  $Li_2B_1$   $_0Cl_{10}$  oxidation by a constant potential electrolysis. We oxidized  $Li_2B_1_0Cl_1_0$  at a Pt foil electrode at 1.62V vs the Ag

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pseudoreference electrode in a stirred solution. After a few minutes of electrolys is, purple material streamed from the Pt electrode. The current declined during electrolysis to a very low level. For the first experiment n was  $1.5$ , a second experiment gave  $n = 2.5$ . In a third experiment we pre-oxidized the acetonitrile solvent to destroy oxidizable impurities before electrolysis. The third experiment gave  $n = 1.0$  to confirm the one electron stoichiometry of the reaction. We characterized this purple, soluble, oxidation product by the UV-VIS spectrum shown in Figure 12. The material is characterized by two absorption bands in the visible at 569 and 419 nm with more intense bands in the UV. The reaction of the purple species in solution was shown by a decline in absorbance of  $\sim$  10% over a one hour period.

We explored the oxidation chemistry of  $Li_{2}B_{10}Cl_{10}$  further in a series of experiments. We tried cyclic voltammetry on  $\rm Li_2B_{10}Cl_1_0$  in  $\rm CH_2Cl_2/$  $N(bu)$ <sub>4</sub> ClO<sub>4</sub>, but found that  $Li_2B_{10}Cl_{10}$  was insoluble. We then prepared (N (pr)<sub>4</sub>)<sub>2</sub>  $B_{10}Cl_{10}$  by metathesis with N(pr)<sub>4</sub>Br. The salt  $(N(pr)_4)_2B_{10}Cl_{10}$  was soluble in  $\mathrm{CH}_2\mathrm{Cl}_2$  and was characterized by cyclic voltammetry. In  $\mathrm{CH}_2\mathrm{Cl}_2$  the  $\mathrm{B}_{10}\mathrm{Cl}_{10}$ anion behaved similarly to  $\mathtt{CH}_3\textrm{CN}$  except that the second, irreversible wave could not be observed because of the limited potential range of  $\mathrm{CH}_2\mathrm{Cl}_2$  .

We also explored chemical methods for generating the oxidation products of  $Li_2B_{10}Cl_{10}$ . In both  $CH_3CN$  and aqueous solution the purple species is formed by addition of Ce<sup>IV</sup> to  $\text{Li}_{2}\text{B}_{10}\text{Cl}_{10}$ . The purple product was concentrated on filter paper and dissolved in  $CH_2Cl_2$ . This product had absorption bands at 573 and 421 nm, only slightly shifted from  $\overline{\text{CH}}_{3}\text{CN}$ . We tried to isolate the purple product  $\texttt{LiB}_{10}\texttt{Cl}_{10}$  by evaporating  $\texttt{CH}_{2}\texttt{Cl}_{2}$ , but were unsuccessful.

The second oxidation product in  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  occurs at a very high potential  $4.5 + V$  vs. Li and cannot easily be studied by cyclic voltammetry. We decided to use normal pulse (npp) and differential pulse (dpp) polarography to minimize the effect of the background current and allow the oxidation to be clearly resolved. The polarograms were taken at a platinum electrode since mercury was oxidized at the high anodic potentials required. The normal pulse polarogram for  $Li_2B_{10}Cl_{10}$  in  $CH_3CN/N(bu)_4ClO_4$  is shown in Figure 13. As

shown in the figure, the slight  $Cl^{-}$  impurity shows up as a polarographic maxima while both the first and second waves are quite clearly defined. In the npp the second oxidation wave is still in the ris ing baseline, but appears to be higher than the first oxidation. The picture presented by the oxidation product of  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  is clarified by use of differential polarography (dpp) as shown in Figure 14. The dpp reveals the initial impurity wave followed by two supcessive symmetric peaks, indicative of reversible processes. The peak heights, 50 and  $51 \mu$ A respectively show that both are one electron oxidations. There were no further oxidation processes out to  $+2.8V$ . The apparent half wave potentials of 1.43 and 2.16V are comparable to potentials estimated by cyclic voltammetry.

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In the electrochemicaland chemical experiments we demonstrated that the supporting salt  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  undergoes two reversible diffusion controlled one electron oxidations. The product of the first of these oxidations,  $\text{LiB}_{10}\text{Cl}_{10}$ was characterized by its UV-VIS spectrum with strong absorbances at 569 and 419 nm in  $CH<sub>3</sub>CN$  solution.

#### IV. Conclusion

As required in the work statement for this contract, we developed a hermetically sealed prototype rechargeable D cell with reference electrode by modifying a conventional primary Li/SO<sub>2</sub> cell to incorporate a second G/M seal feedthrough for the Li reference. This allowed us to maintain the standard filling and venting arrangements for  $\rm Li/SO_{2}$  cells intact. We filled these cells with the experimental  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SO}_2$  all inorganic electrolyte and roughly characterized primary cell performance. We used selected D cells with reference electrode for chemical analysis and demonstrated the. quantitative formation of  $\rm{Li}_{2} \rm{S}_{2} \rm{O}_{4}$  in the cathode during cell discharge as well as the quantitative oxidation of  $\text{Li}_2\text{S}_2\text{O}_4$  to  $\text{SO}_2$  during cell recharge. This established the rechargeable nature of the positive electrode reactions.

We investigated the chemistry of the supporting salt  $\mathrm{Li}_2\mathrm{B}_{10}\mathrm{Cl}_{10}$ during recharge and found that  $\rm Li_2B_{10}Cl_{10}$  is oxidized in two one electron processes at high voltage [13J. Only the first oxidation process at 3.6V

$$
B_{10}Cl_{10} \xrightarrow{2-3.6V} B_{10}Cl_{10} \xrightarrow{4.2V} B_{10}Cl_{10} \qquad [13]
$$

vs. Li is reached during cell recharge. The initial oxidation product is a pers istent material characterized by absorbances at 569 and 419 nm.

We demonstrated both the inherently high energy density and rechargeable nature of the Li/SO<sub>2</sub> system using the exotic electrolyte salt Li<sub>2</sub>B<sub>10</sub>Cl<sub>10</sub>.

This report includes information concer ning proprietary property of Duracell International Inc., and the presence of any information herein should not be interpreted to mean that the technology described was or was not developed pursuant to any government financed project.

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Table 1



Weights and Cell Capacities of Prototype Rechargeable D Cells

### TABLE 2



## Chemical Analysis of D Cells

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, Current/Potential Data for Cyclic Voltammograms of  $\mathrm{Li}^{-\mathrm{B}}_{2.2}\mathrm{Cl}_{2.2}$  $2^-10^-10$ 





Figure 1. CRS can used for  ${SO_2}$  cells showing the convoluted vent and  $\tilde{f}$ ill eyelet  $\tilde{f}$ 





# **WOUND CELL**

Figure 2. Side view of a standard LO26S SO<sub>2</sub> cell.



# REFERENCE CELL TOP

Figure 3. Cell top incorporating referenced electrode feedthrough



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Figure 4. Voltage vs. time behavior for a rechargeable D cell at 0.3A discharge; both anode and cathode potential vs. the lithium reference are shown.

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Figure 5. Voltage vs, time behavior for a rechargeable D cell at 0.3A discharge; both anode and cathode potential vs. the lithium reference are shown



Figure. 6.. Voltage vs. time behavior for the cell in Fig. 5 during recharge at 0.3A; both anode and cathode potential vs. the lithium reference are shown.











Figure 9. Cyclic voltammograms of  $L1_2B1_0CI1_0$  in  $CE_3CN/N(bu)_4ClO4$ <br>at 200 mV/sec.







Figure 11. Plot of peak anodic current  $I_{pa}$  vs.  $\sqrt{V}$ , root of sweep rate for<br> $U_2E_1eCl_1n$  in acctonitrile showing diffusion control.

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