

## Short Communication

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### Differential Scanning Calorimetry Studies of Possible Explosion-Causing Mixtures in Li/SO<sub>2</sub> Cells

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#### Introduction

Batteries based on the Li/SO<sub>2</sub> electrochemical couple are being developed for many applications requiring high energy density power sources. However, there have been many hazards to safety associated with this system in which cells have either vented, caught fire or exploded [1]. Since the explosion hazard may be attributable to exothermic reactions occurring among cell components and/or products of discharge, thermal studies were undertaken in an effort to identify reactions that could initiate or produce an explosive combustion. This initial qualitative investigation was restricted to chemical combinations involving the lithium anode material.

#### Experimental

A DuPont Model 990 differential scanning calorimeter (d.s.c.) was employed to measure changes in enthalpy and temperature in sample mixtures heated at a programmed rate, usually 10 °C/min, under a flowing atmosphere of dry argon. All samples were weighed, mixed and hermetically sealed in an Armco iron d.s.c. cell in a dry room maintained at 2% relative humidity. Solid materials were vacuum dried, and the moisture content was checked by d.s.c. and by thermogravimetric analysis (t.g.a.). The solids were folded in a single piece of lithium (99.9%, Foote Mineral Co.) and firmly pressed together. Anhydrous SO<sub>2</sub> was condensed under argon. Acetonitrile was triply distilled [2]. Mixtures involving volatile liquids were studied employing stainless-steel Perkin-Elmer large volume (75 μl) capsules with O-ring seals. Multiple runs were performed on all mixtures.

#### Results and discussion

Although several solute (LiBr, LiAsF<sub>6</sub>)-solvent (CH<sub>3</sub>CN, propylene carbonate) combinations are employed in the Li/SO<sub>2</sub> battery system, our atten-

TABLE 1  
Summary of d.s.c. results

Run number	Reactants	Temperature (°C)†	
		Endothermic transitions	Exothermic transitions
1	Li	181	-
2	LiAsF <sub>6</sub>	258	-
3	LiAsF <sub>6</sub> ·H <sub>2</sub> O	117, 258	-
4	Li + Shawinigan black	181	-
5	Li + polypropylene	160, 181	-
6	Li + propylene carbonate	181	-
7	Li + Li <sub>2</sub> SO <sub>3</sub>	181	445
8	Li + LiAsF <sub>6</sub> ·4CH <sub>3</sub> CN	60	121(+13), 180(+7)
9	Li + LiBr	181	142(+7)
10	Li + CH <sub>3</sub> CN + LiAsF <sub>6</sub>	87, 181	221(+15)
11	Li + LiAsF <sub>6</sub> + propylene carbonate	181, 226*	216
12	Li + CH <sub>3</sub> CN	117*	97
13	Li + CH <sub>3</sub> CN + propylene carbonate	176*	171
14	Li + CH <sub>3</sub> CN + S + SO <sub>2</sub>	117, 154*	147
15	Li + CH <sub>3</sub> CN + LiAsF <sub>6</sub> + SO <sub>2</sub>	179*	178
16	Li + Li <sub>2</sub> SO <sub>3</sub> ·H <sub>2</sub> O	181	83, 137(+5)
17	Li + Li <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (wet)	180	107, 152, 244(+2)
18	Li + Li <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (dry)	181	152(+12), 239, 244(+203)
19	Li + Teflon	180	185(+2), 261(+87)
20	Li + LiAsF <sub>6</sub> + LiAsF <sub>6</sub> ·H <sub>2</sub> O	180	78, 160(+7), 214(+3), 246(+140)
21	Li + LiAsF <sub>6</sub>	181	216(+179)
22	Li + S	118, 180	142(+120)
23	Li(SO <sub>2</sub> film) + S	117, 181	124(+305)

†Temperature increase in the d.s.c. sample cell associated with exothermic transitions is indicated in parentheses.

\*Pressure burst.

tion was focused primarily on the  $\text{LiAsF}_6\text{-CH}_3\text{CN}$  electrolyte. Table 1 summarizes some of the d.s.c. studies performed on various chemical combinations of cell components and/or potential discharge products. The values reported are the observed initiation temperatures of endothermic and exothermic transitions. Sudden large increases in the temperature of the sample cell that were observed for some of the samples are shown in parentheses following the temperature of the exothermic transition. A few of the more energetic reactions are illustrated in the d.s.c. curves in Fig. 1. Detailed results are reported elsewhere [3]. A brief discussion of Table 1 follows.

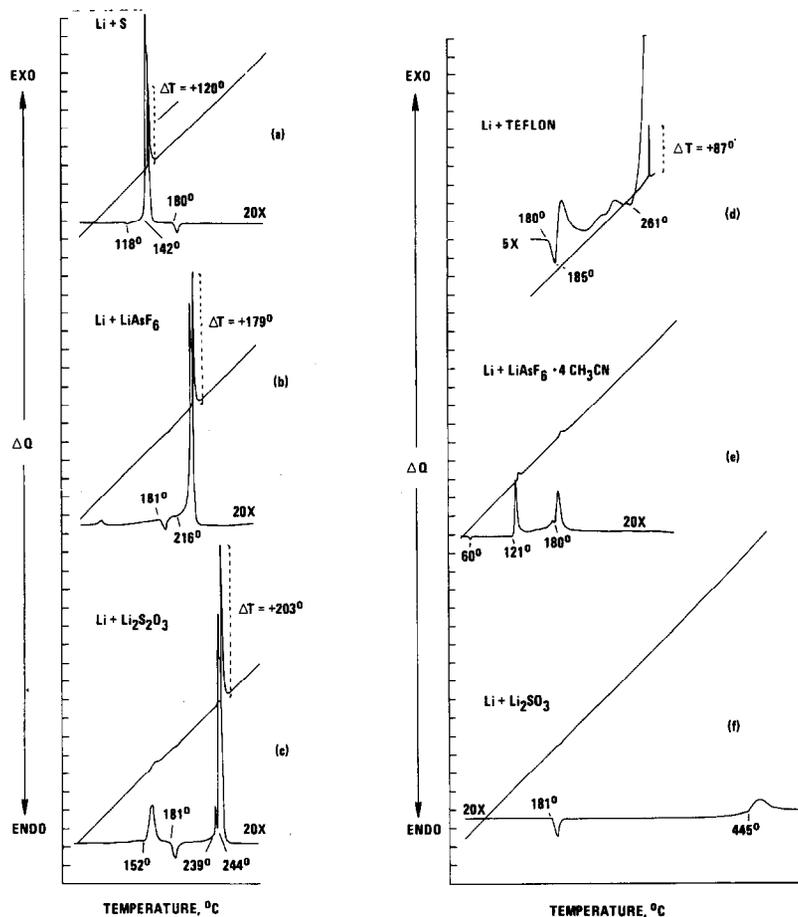


Fig. 1. Differential scanning calorimetry curves. (a) Lithium (2.70 mg) + sulfur (2.20 mg); (b) lithium (1.90 mg) +  $\text{LiAsF}_6$  (5.00 mg); (c) lithium (3.40 mg) +  $\text{Li}_2\text{S}_2\text{O}_3$  (6.50 mg); (d) lithium (1.60 mg) + Teflon (4.20 mg); (e) lithium (2.00 mg) +  $\text{LiAsF}_6 \cdot 4\text{CH}_3\text{CN}$  (wet with  $\text{CH}_3\text{CN}$ ); (f) lithium (3.90 mg) +  $\text{Li}_2\text{SO}_3$  (3.60 mg).

$\text{LiAsF}_6$  undergoes a reversible phase transition at  $258^\circ\text{C}$ . The presence of moisture is indicated by an endotherm at  $117^\circ\text{C}$  corresponding to dehydration of the monohydrate. Several combinations (runs 4 - 7) produced no

exothermic reactions on heating to 300 °C or produced only minor exotherms (runs 8 - 17). Two of the mixtures, lithium-Teflon (run 19) and Li-LiAsF<sub>6</sub>·4CH<sub>3</sub>CN [4] (run 8) were not reproducible. Generally, Teflon was either non-reactive or slowly reactive, characterized by broad exotherms. However, an energetic reaction between lithium and Teflon was observed and is illustrated in Fig. 1(d). The reaction of lithium with LiAsF<sub>6</sub>·4CH<sub>3</sub>CN (wet with CH<sub>3</sub>CN) may have been dependent on the amount of excess CH<sub>3</sub>CN present. Attempts to prepare dry LiAsF<sub>6</sub>·4CH<sub>3</sub>CN by vacuum drying at 25 °C appeared to give mixtures of lower solvates as evidenced by t.g.a. studies.

The unexpected but reproducible exotherm obtained from mixtures of lithium with lithium bromide (vacuum dried extensively at 210 °C) may be the result of the deliquescent nature of LiBr.

The thermal behavior of lithium with another common solute, LiAsF<sub>6</sub>, was recorded in triplicate. Explosive exotherms were initiated at approximately 197 °, 216 °, and 236 °C accompanied by sample cell increases of 177 °, 179 °, and 36 °C, respectively. Typical behavior is illustrated in Fig. 1(b). The effect of moisture was studied by preparing a Li-LiAsF<sub>6</sub> mixture containing some LiAsF<sub>6</sub>·H<sub>2</sub>O (run 20). Small exotherms were observed with an explosive combustion occurring at approximately 246 °C accompanied by a 140 °C increase in cell temperature.

Typical thermal behavior of lithium with possible cell discharge or decomposition products such as sulfur, thiosulfate, and sulfite are illustrated in Figs. 1(a), (c), and (f), respectively. Although consistently reproducible, the non-reactive behavior of lithium with anhydrous sulfite (run 7) and the small exotherms with the sulfite monohydrate contrasts with another recent thermal analysis study [5, 6]. The anhydrous sulfite exhibits thermal decomposition by an exotherm at approximately 445 °C and lacks the 145 °C endotherm characteristic of the dehydration of the monohydrate.

Figure 1(a) illustrates the violent nature of the lithium-sulfur reaction when "wetting" occurs. Examination of the 118 °C endotherm with increased sensitivity revealed two endotherms corresponding to the melting of two forms of sulfur, followed by explosive combustion at 142 °C that results in a 120 °C increase in cell temperature. The endotherm at 181 °C corresponds to the fusion of excess unreacted lithium. If the reactants do not "wet", initiation of a similar exotherm is delayed until 235 °C and is accompanied by a temperature increase of 73 °C.

The reactivity of sulfur with lithium containing a protective film was investigated in order to simulate battery conditions. Lithium (2.00 mg) was pressed to a large surface area and immersed in dry liquid SO<sub>2</sub> for 15 min until a 0.30 mg film formed on the lithium. Sulfur (5.05 mg) was then folded inside the coated lithium and a d.s.c. curve similar to Fig. 1(a) was obtained. The melting of sulfur appeared to initiate the reaction, increasing the sample cell temperature from 124 ° to 429 °C.

Figure 1(c) is an example of the very reproducible d.s.c. curves obtained upon heating lithium with very dry Li<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Thiosulfate containing moisture

(run 17) gives rise to an additional exotherm at approximately 107 °C. However, an explosive combustion was not observed.

Studies involving volatile liquid components were limited by endothermic pressure bursts of the O-ring cell (runs 11 - 15). The bursts appeared to be initiated by an exothermic reaction and prevented the meaningful measurement of increases in cell temperature.

Propylene carbonate (PC) is often used as a co-solvent with acetonitrile. Lithium-acetonitrile mixtures produced non-explosive but very exothermic reactions. No exothermic reaction was observed from 25 ° to approximately 171 °C when PC was added to the mixture (run 13). It appears that a protective film, possibly  $\text{Li}_2\text{CO}_3$ , prevents reaction until temperatures approaching the fusion of lithium are attained. Propylene carbonate by itself does not, however, prevent the very exothermic reaction between lithium and  $\text{LiAsF}_6$ . Explosive combustion still occurs at 216 °C, with the temperature increase unmeasurable due to an ensuing endothermic pressure burst.

The behavior of lithium- $\text{CH}_3\text{CN}$ - $\text{SO}_2$  mixtures containing sulfur (run 14) and  $\text{LiAsF}_6$  (run 15) were investigated. The absence of low temperature exotherms verifies that  $\text{SO}_2$  prevents reaction between lithium and  $\text{CH}_3\text{CN}$ . The  $\text{SO}_2$  did not prevent the violent lithium-sulfur exotherm. The mixture containing  $\text{LiAsF}_6$  was non-reactive up to temperatures approaching the fusion of lithium, whereupon reaction initiated a pressure burst of the O-ring cell. Isothermal heating at 130 °C for 15 minutes produced no exothermic reaction. Preliminary studies using welded cells indicate that the violent lithium- $\text{LiAsF}_6$  reaction previously observed may not occur in mixtures containing  $\text{CH}_3\text{CN}$  and  $\text{SO}_2$ .

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