

Safety study of electrolyte solutions for lithium batteries by accelerating-rate calorimetry

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Introduction

Recalls of lithium batteries due to an overheating defect in 1989 have caused a widespread interest in the safety concerns of Li batteries [1]. Our company, a supplier of electrolyte solutions, has since been paying attention to such problems.

Electrolyte solutions used for Li primary batteries, especially for customer use, are mainly composed of lithium perchlorate (LiClO_4) or lithium trifluoromethanesulfonate (LiCF_3SO_3) as a solute and a mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) as a solvent.

We have investigated the thermal stability of these electrolyte solutions with and without electrode materials using an accelerating-rate calorimeter (ARC), an instrument developed for the thermal hazard analysis of flammable materials in adiabatic conditions.

Experimental

The ARC, a computer-controlled highly-adiabatic calorimeter, was obtained from Columbia Scientific Industries, Inc. When an exothermic reaction is detected, it maintains the sample in adiabatic conditions and continuously monitors its thermal and pressure behaviors. Figure 1 shows a schematic drawing of the ARC. More details for ARC are cited in refs. 2-4.

The electrolyte solutions used were LiClO_4 and LiCF_3SO_3 (1 M) in PC and DME equivolume mixture. Electrode materials used were lithium metal (Li) and manganese dioxide (MnO_2). Table 1 shows the summary of tested samples.

ARC experiments were conducted under the following conditions: (i) start temperature 40 °C; (ii) end temperature 400 °C; (iii) slope sensibility 0.02 °C/min; (iv) heat step 3 °C, and (v) wait time 15 min.

Results and discussion

Tables 2 summarizes the experimental results. Figures 2-5 show the heat rate versus temperature plots of each cases. Figures 6-9 show the pressure versus temperature plots.

The LiClO_4 solution, decomposed immediately after the exothermal reaction, was observed at 217 °C. MnO_2 caused the LiClO_4 solution to be more unstable, lowers the observed onset temperature and raises the maximum self-heat rate. Lithium caused the solution to be even more unstable than MnO_2 . Because of the intense increase

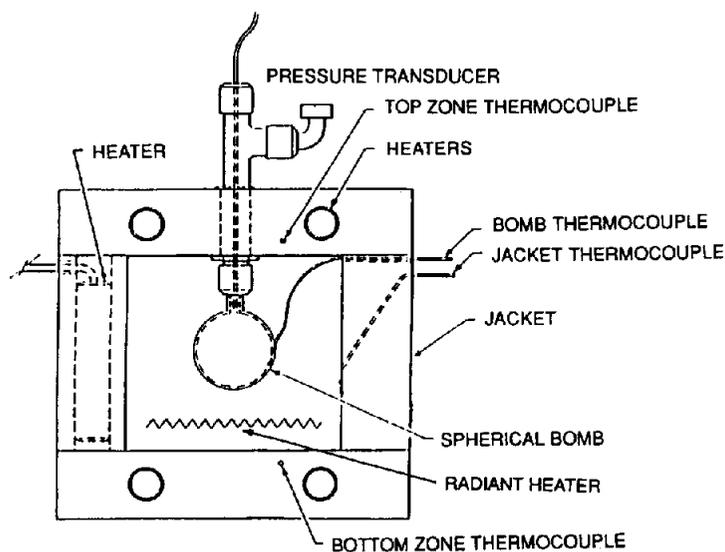


Fig. 1. A schematic drawing of the accelerating-rate calorimetry.

TABLE 1

List of tested materials by the accelerating-rate calorimetry

Sample	Electrolyte		Lithium metal (g)	Manganese dioxide (g)
	Composition	(g)		
A	PC+DME	1.69	none	none
B	LiClO ₄ /PC+DME	1.67	none	none
C	LiCF ₃ SO ₃ /PC+DME	1.68	none	none
D	PC+DME	1.12	0.05	none
E	LiClO ₄ /PC+DME	1.30	0.04	none
F	LiCF ₃ SO ₃ /PC+DME	1.13	0.04	none
G	PC+DME	1.10	none	1.09
H	LiClO ₄ /PC+DME	1.13	none	1.11
I	LiCF ₃ SO ₃ /PC+DME	1.05	none	1.04
J	PC+DME	1.37	0.05	0.61
K	LiClO ₄ /PC+DME	1.47	0.05	0.66
L	LiCF ₃ SO ₃ /PC+DME	1.44	0.05	0.66

in the pressure, the ARC system shut down. We consider the LiClO₄ solution to be extraordinarily dangerous when it is heated in a closed vessel with electrode materials, especially Li metal.

On the other hand, the LiCF₃SO₃ solution showed a moderate behavior compared with the LiClO₄. Its maximum self-heat rate was lower than 4 °C/min, 1/60 of that with LiClO₄.

TABLE 2
Temperature and pressure behavior for exotherms detected in the tested samples

	Sample											
	A	B	C	D	E	F	G	H	I	J	K	L
Observed onset temperature (°C)	265	217	268	185	149	155	132	138	144	187	173	171
Self-heat rate at onset temperature (°C/min)	0.04	0.04	0.02	0.18	0.02	0.02	0.02	0.02	0.02	0.22	0.05	0.03
Adiabatic temperature rise (°C)	4.08	111	> 132	136	> 56.7	151	132	183	123	172	> 81.1	191
Final adiabatic temperature (°C)	269	328	> 400	321	> 206	306	251	322	266	359	> 294	362
Maximum self-heat rate (°C/min)	0.56	208	3.61	81.0	> 143	13.9	19.2	343	12.3	32.8	> 9.3	6.63
Temperature at maximum rate (°C)	267	314	400	242	> 206	196	229	241	218	312	> 254	329
Pressure at maximum rate (kg/cm ²)	18.9	101	129	30.8	> 229	11.5	38.2	84.7	31.8	47.0	> 229	25.6
Maximum observed pressure (kg/cm ²)	20.9	101	130	55.8	*	44.2	39.9	78.8	35.2	55.7	*	28.1
Maximum observed temperature (°C)	265	314	400	321	*	306	251	241	266	357	*	356
Heat of reaction (cal/g)		> 157	162	204	*	70	111	113	234	178	*	193
Time to maximum rate (min)		440	420	9.4	60	420	570	300	60	11	53	120

*Data were not obtained because of the shut down of ARC system by the pressure higher than setup value.

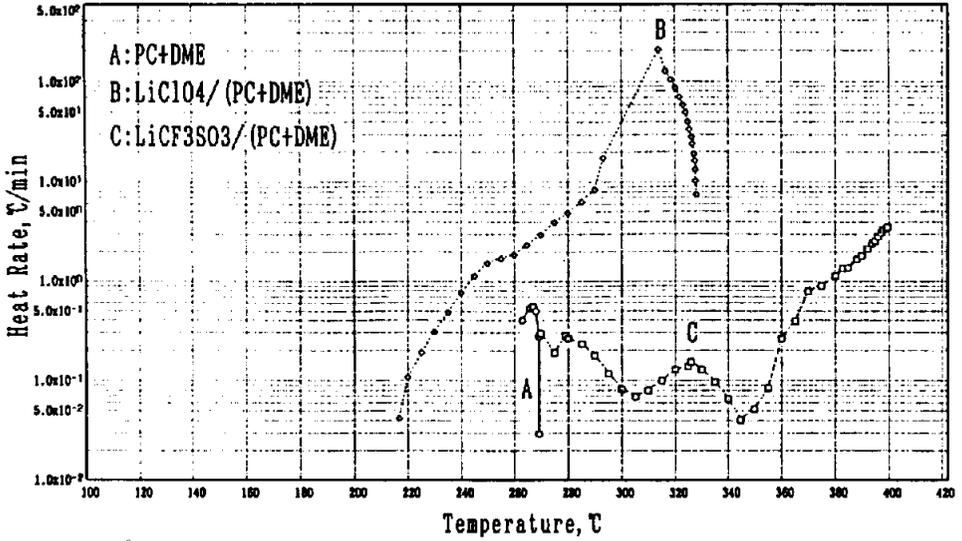


Fig. 2. Heat rate vs. temperature plot of the electrolytes without electrode materials.

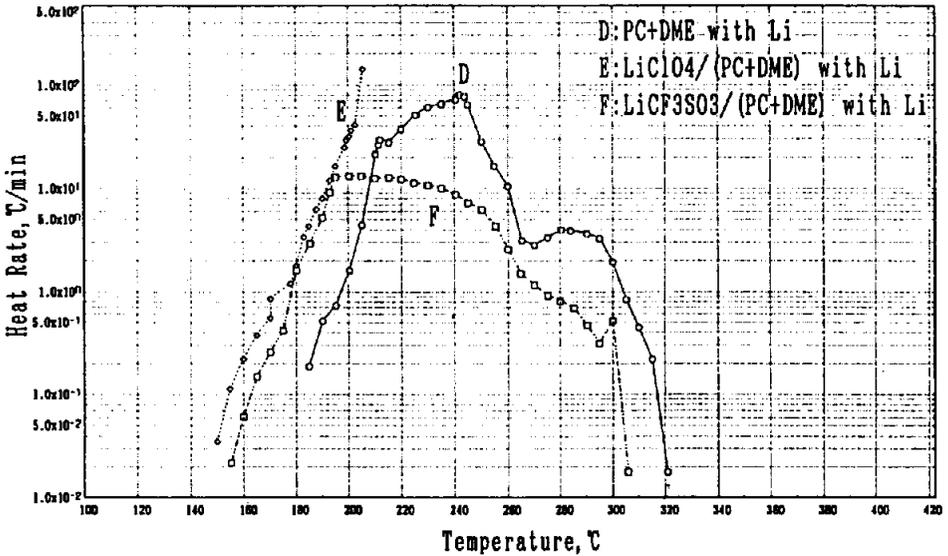


Fig. 3. Heat rate vs. temperature plot of the electrolytes with lithium.

The exothermic reaction occurred very slowly and consecutively. Either electrode, MnO₂ and Li, lowered the thermal stability, similarly, as the case of LiClO₄. The maximum self-heat rate of the solution with LiCF₃SO₃, however, was low, 14 °C/min, 1/10 of that with LiClO₄. The maximum observed pressure was also low.

In the case of the solvent without a solute, the maximum self-heat rates of the solvent were smaller than those with LiClO₄, and larger than those with LiCF₃SO₃. The levels of the reaction heat were similar in all cases. We suppose these effects

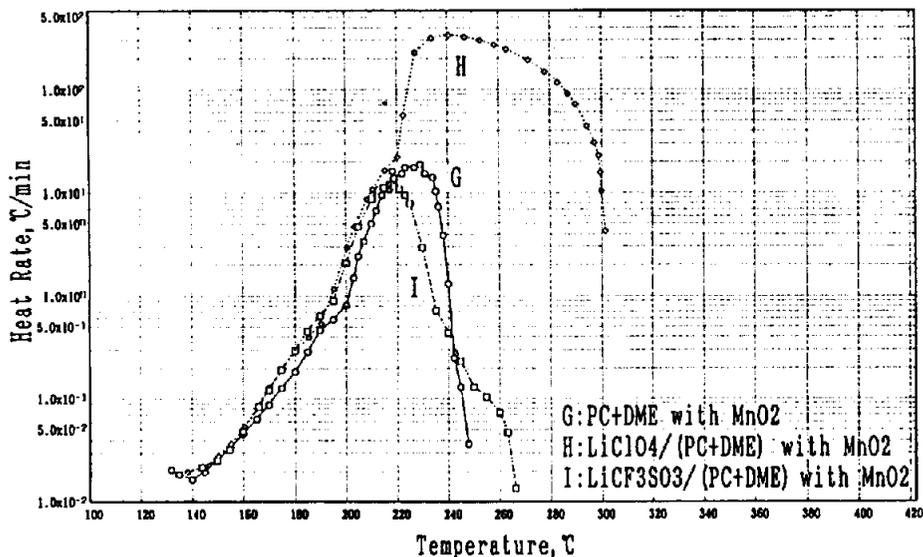


Fig. 4. Heat rate vs. temperature plot of the electrolytes with manganese dioxide.

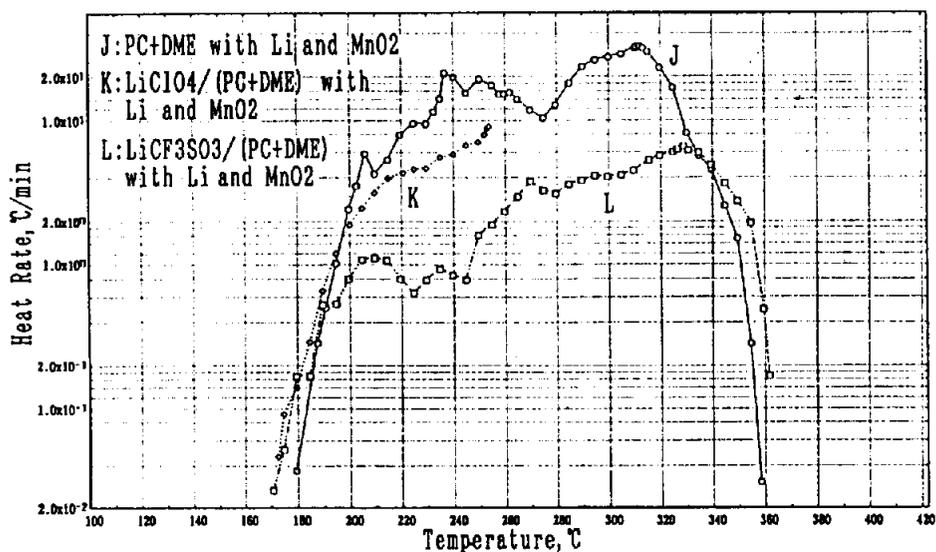


Fig. 5. Heat rate vs. temperature plot of the electrolytes with lithium and manganese dioxide.

are deeply concerned with the decomposition mechanism of these salts: LiClO₄ decomposes into LiCl and O₂ at 440 °C, and LiCF₃SO₃ decomposes into LiF, SO₂ and COF at 420–480 °C.

We consider the exothermic reactions to be mainly caused by the decomposition of the solvent with electrode materials, and they are accelerated by LiClO₄, and retarded by LiCF₃SO₃.

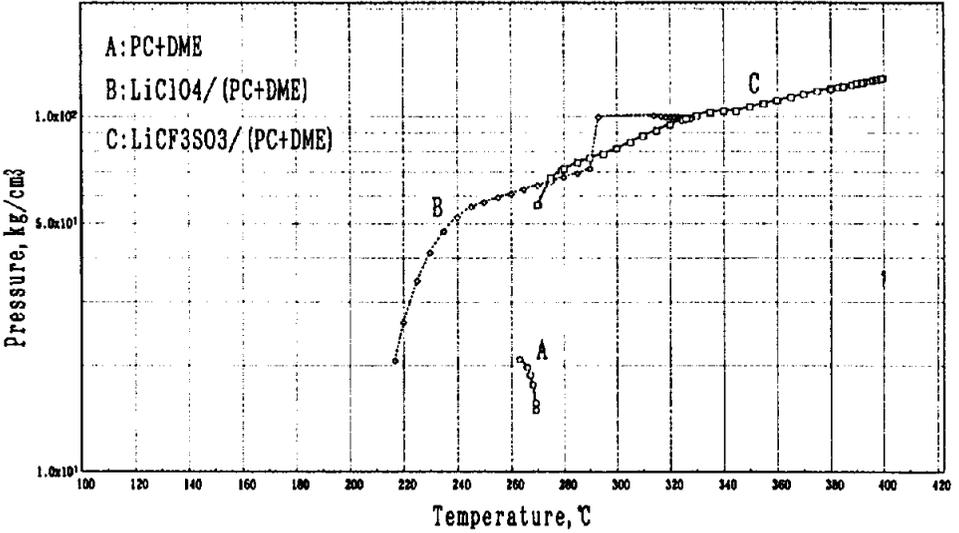


Fig. 6. Pressure vs. temperature plot of the electrolytes without electrode materials.

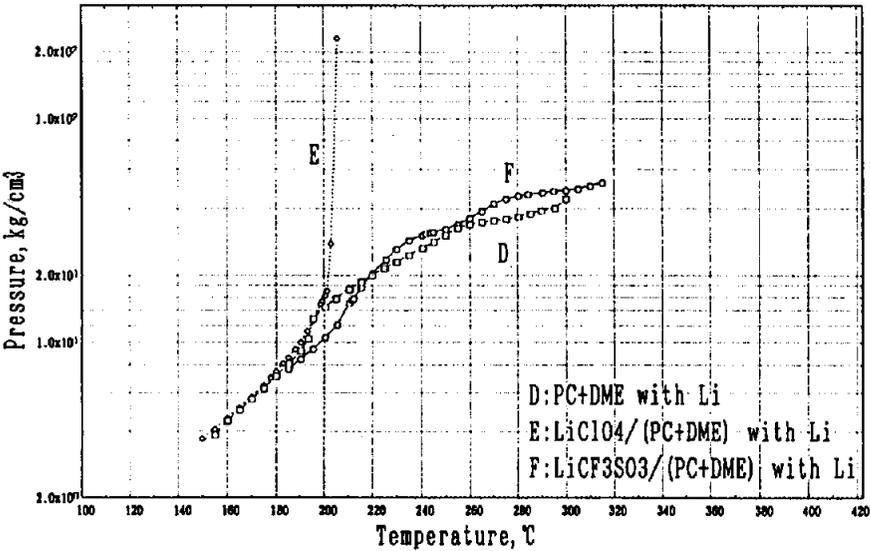


Fig. 7. Pressure vs. temperature plot of the electrolytes with lithium.

Conclusion

Electrode materials, MnO₂ and Li, have a tendency to unstabilize the electrolyte solutions. LiClO₄ accelerated the exothermic reaction of the electrolyte solutions, but LiCF₃SO₃ retarded them. Thus, we conclude that LiCF₃SO₃ is a more favorable electrolyte than LiClO₄ from the safety views of Li batteries.

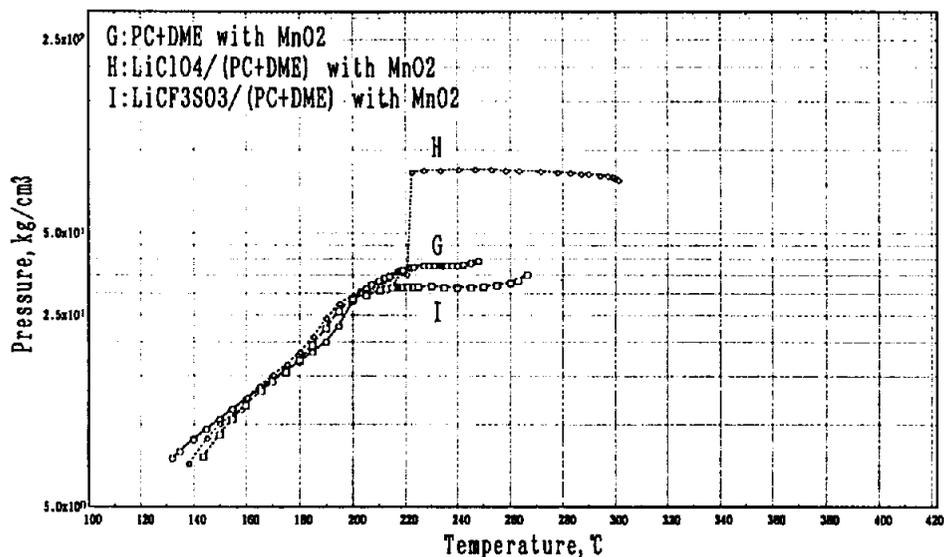


Fig. 8. Pressure vs. temperature plot of the electrolytes with manganese dioxide.

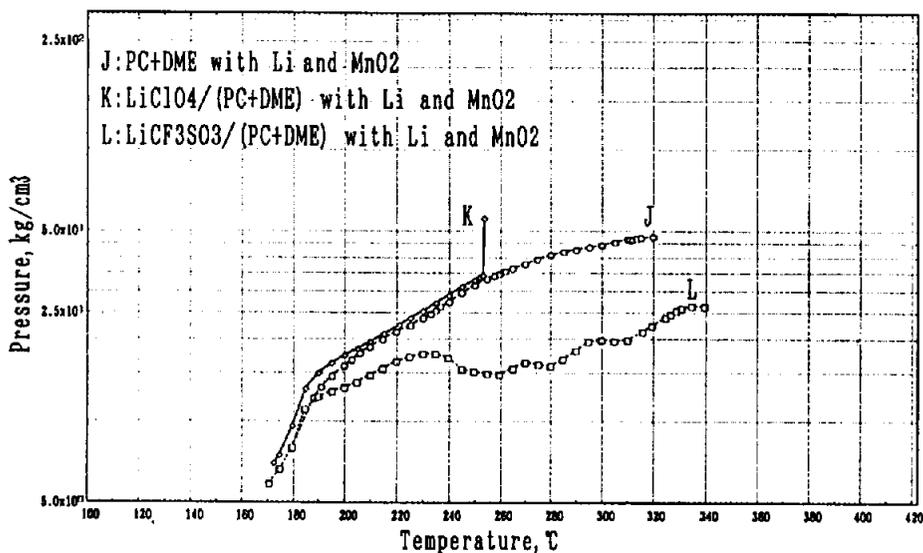


Fig. 9. Pressure vs. temperature plot of the electrolytes with lithium and manganese dioxide.

References

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