Effects of cathode materials on discharge characteristics of Li-B alloy/ FeS$_2$ thermal battery[①]

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Abstract : The effects of FeS$_2$ on the discharge characteristics of Li-B alloy/ FeS$_2$ thermal battery had been studied . Results showed that 2 .5 %(mass fraction) Li$_2$O would be needed to rule out the voltage pulse in the first part of discharge curves for the FeS$_2$ powder of small particle size (< 44 μm) . After thermal decomposition , the FeS$_2$ had transformed to Fe$_{(1-x)}$S where $x = 0 .024 \sim 0 .066$. The deficiency of the cathode FeS$_2$ would make discharge voltage decrease 0 .4 V . In the discharge test at high temperature (600 ℃) , the discharge voltage decreased fast with the acceleration of the thermal decomposition of FeS$_2$.

Key words : LiB ; FeS$_2$; thermal batteries ; cathode effect   **Document code : A**

1 INTRODUCTION

In general , FeS$_2$ is taken as cathode material to form molten salt battery with most advanced anode materials Li-B alloys[1] . Evidently , the state of FeS$_2$ has corresponding effects on the discharge characteristics of Li-B/ FeS$_2$ molten salt batteries . Investigation on this problem will be meaningful to stabilization of behavior of Li-B/ KCl- LiCl/ FeS$_2$ series batteries and constitution of corresponding standard test method . In this paper , relative experiment phenomenon about discharge test of Li-B/ KCl- LiCl/ FeS$_2$ molten salt batteries has been summarized and investigated .

2 EXPERIMENTAL

2 .1 Preparation of Li-B anode pellet

The nominal composition of Li-B anode was B-67 % Li , where Li was pure Li ingot , purity 99 .9 % , B is amorphous boron , purity ≥90 % .

The Li-B alloy ingot , whose phase composition was Li + Li$_7$B$_6$ + Li$_2$O (a little) , was synthesized in iron crucial . After mechanical heat treatment , the Li-B alloy ingot was rolled into thin film with thickness of 0 .31 ~ 0 .35 m m in dry air , then the anode pellet of 1 7 .5 m m in spherical diameter was stamped .

2 .2 Preparation of electrolyte/ cathode pellet

Electrolyte powder

The mixture powder (mass fraction , %) 60 (45 LiCl + 55 KCl) - 40 MgO was mixed , melted , ground and sieved through 100 mesh

Cathode powder

FeS$_2$: Natural pyrite is ground and sieved through 320 mesh .

Fe$_{0 .96}$S : FeS$_2$ powder was kept in vacuum at 750 ℃ for 5 h and then cooled .

Li$_2$O : Chemical purity LiOH · H$_2$O was dried in vacuum at high temperature , ground and sieved through 200 mesh . Cathode powder was prepared by mixing the above powders

according to certain proportions (Table 1) .

Table 1   Composition of cathode powder
(mass fraction , %)

No	FeS$_2$	Fe$_{0.96}$S	Electrolyte powder	Li$_2$O	
1	70		30		
2		70	30		
3	69 .0		29 .6		
4	68 .6		29 .4	1 .5	
5	68 .3		29 .3	2 .0	
6	69 .0		29 .6	1 .5	400 ℃ , 15 h
7	68 .3		29 .3	2 .5	400 ℃ , 15 h

Electrolyte/ cathode pellet : In the steel mould , 0 .4 ~ 0 .5 g cathode powder was put on the bottom and the upside was the ~ 0 .1 g electrolyte powder . Electrolyte/ cathode pellet was prepared by pressing with pressure 160 ~ 200 MPa .

2 .3 Discharge test

Li- B anode/ electrolyte/ cathode pellets were clipped with pure nickel pellets and sent into a heated stainless steel pressing clumps in which there was a little resistance furnance . The discharge was undergone in galvanostatic mode at temperature 500 , 520 , 550 and 600 ℃ , with current density 200 mA/ cm^2 .

3   RESULTS

3 .1   Preparation of Fe$_{0.96}$S

After vacuum heat treatment , the color of the FeS$_2$ powder changed from yellow brown to black brown , the iron container became thick and fragile . XRD spectra of the powder is shown in Fig .1 . Before treatment the phase composition was mainly FeS$_2$ and some FeSO$_4$·H$_2$O , after treatment FeS$_2$ transforms to Fe$_{1-x}$S and FeSO$_4$·H$_2$O transforms to Fe$_3$O$_4$. According to the recent published PDF File[2] , there are 19 kinds of iron sulfide . The Fe$_{1-x}$S in our experiment is pyrrhotite (20 ~ 534) , where x = 0 .024 ~ 0 .066 , the proportion is near to FeS . This kind of product is more near to the practice where FeS$_2$ has to experience thermal decomposition at

high temperature .

Fig .1   X- ray spectra of FeS$_2$
(a) —Raw materials ; (b) —Vacuum heat treated
(750 ℃ , 14 h)
○ —FeS$_2$;   ▲ —FeSO$_4$·H$_2$O ;
● —Fe$_{1-x}$S(x = 0 .024 ~ 0 .066) ;   △ —Fe$_3$O$_4$

3 .2   Discharge test results

Fig .2 is the discharge curves where 1 .5 , 2 .0 , 2 .5 %(mass fraction , %) LiO$_2$ have been added to the cathode materials . Results show that the first peak has been eliminated but no evident effect on discharge specific capacity when

Fig .2   Discharge curves with the addition of
Li$_2$O to cathode material
1 —0 %Li$_2$O; 2 —1 .5 %Li$_2$O;
3 —2 .0 %Li$_2$O; 4 —2 .5 %Li$_2$O

the addition quantity of LiO_2 is up to 2 . 5 % . Fig . 3 is the discharge curve where the 1 . 5 , 2 . 5 % Li_2O have been added and the cathode mixture powder has been heat treated . Results show that the first peak has not been eliminated for the 1 . 5 % Li_2O addition , but has been eliminated so much for the addition of 2 . 5 % Li_2O , at the same time the discharge activation has been delayed .

Fig . 4 is the discharge curves that $Fe_{0.96}S$ has been taken as cathode materials . It shows that the peak still exists but narrower than that of taking FeS_2 as cathode materials , the

discharge plateau is long and plain , and the discharge voltage is 0 . 4 V lower than that as taking FeS_2 as cathode . There is no second discharge plateau in the curve .

Fig . 5 is the discharge curves at different temperature using 1 [#] cathode materials . The curve of 500 ℃ is near to that of 550 ℃ , but at 600 ℃ , the first discharge plateau shortens , discharge voltage increases and the second discharge plateau extends .

Fig . 5   Discharge curves at different temperature

4   DISCUSSION

Comparing the discharge curves that no Li_2O has been added to the cathode materials with that of Szwarc' s results(Fig . 6) , the first peak in our curves is high and broad . The first peak in the discharge curve is related to the surface area of the FeS_2 powder[3] . In general , 1 . 5 % Li_2O added to cathode materials is enough to eliminate the first peak[4] , however , in our experiment , 2 . 5 % Li_2O is needed (Fig . 2) . If the cathode mixture powder is roasted at 400 ℃ for 1 5 h[4] , the effect of the Li_2O will be enhanced .

The discharge curves of Li-B/ FeS_2 cell are different from each other for the different discharge conditions . Fig . 6 has two evident plain

Fig . 3   Effects of roasting cathode powder mixture on discharge curves
1 —0 % Li_2O ; 2 —1 . 5 % Li_2O ; 3 —2 . 5 % Li_2O

Fig . 4   Comparison of discharge curves for different cathode materials

Fig .6   Experiment results of Szwarc[4]
(B-66 %Li)

discharge plateau . Fig .4-1 do not have evident second discharge plateau and Fig .5 - 3 even have large voltage drop and the second plateaus are longer than the first discharge plateaus . The reason mainly comes from the electrochemical process at anode and cathode . Szwarc[5] had proved that the two discharge plateaus in Fig .6 come from Li-B alloy where the potential of FeS₂ is stable . Similar works had also been finished by Sanchez[6], the NMR (nuclear magnetic resonance) experiment showed that the first discharge plateau comes from the discharge of free Li the second discharge plateau comes from the discharge of ion Li in Li₇B₆ matrix . The calculation showed that the ion Li in Li₇B₆ also takes part in the discharge .

The discharge curves of Szwarc (Fig . 6) merely involve the behavior of anode . It was shown that the discharge plateau voltage difference is about 0 .2 V and it is stable for different current density . In the normalized discharge curves (transferring transverse axis from time to discharge specific capacity (C/ g-anode)) , there is no change in the second discharge plateau length , but the first discharge plateau length is shortened for long time (small current density) discharge curves (Figs .6 ~ 1) the discharge loss mainly come from the solution of active Li in Li-Cl + KCl molten salt[7] . In practice , cathode can also result in two discharge plateaus in discharge curves . Roughly speaking , the first is FeS₂ +

$Li^+ \rightarrow FeS + Li_2S$, the second is $FeS + Li^+ \rightarrow Fe + Li_2S$, the first one lead to high discharge voltage but the second one lead to low discharge voltage .

In fact the state of iron sulphide is really complex , the $Fe_{1-x}S$ decomposed from FeS_2 at 700 ℃ should represent a stable state in the series transition $FeS_2 \rightarrow Fe$. As taking $Fe_{1-x}S$ as cathode the voltage will lower 0 .4 V than that as taking FeS_2 as cathode (Fig . 4) , and the discharge plateau is plain , which show that both the potential of cathode and anode is stable . So the voltage drop in Fig . 4-1 is caused by the cathode materials . The reasons include the shortage of FeS_2 and thermal decomposition of FeS_2 . The sharp drop of discharge voltage is the running-out of active Li in anode . Considering the cathode and anode factor , the critical voltage would be lower 0 .4 + 0 .2 = 0 .6 (V) than the first plateau voltage . In the Figs .2 , 3 , the critical voltage is about 1 .2 V , 0 .8 V lower than the first plateau voltage 2 .0 . It shows that beside the reason of cathode and anode , the concentration polarization leads to the voltage drop 0 .2 V . When the discharge temperature is relatively high (600 ℃) (Fig .5-3) , the electrolyte electrical conductivity increases greatly , the concentration polarization decreases greatly , it leads to the discharge voltage increases greatly . Another side is the increased discharge loss which comes from the solution of free Li into molten KCl-LiCl , it leads the to shorten of first discharge plateau . More important is that with the increase of temperature more FeS_2 decomposes to $Fe_{1-x}S$. Because of shortage of FeS_2 the discharge voltage decreases rapidly , the second discharge plateau is even longer than the first discharge plateau . The voltage difference is about 0 .6 V , it includes the contribution of transition of cathode materials $FeS_2 \rightarrow Fe_{1-x}S$ and the transition of anode materials $Li \rightarrow Li+$ (in Li_7B_6 matrix) .

In summary , more Li_2O is needed for the fine particle FeS_2 in cathode materials to eliminate the first discharge peak . Roasting the cathode mixture powder at 400 ℃ can lower the addition quantity of Li_2O . There are many state in the transition of iron sulphide from FeS_2 to Fe .

$Fe_{0.96}S$ is a kind of relative stable products at about 700 ℃ . The discharge curves of Li-B/ $Fe_{0.96}S$ cell is plain , its discharge voltage is 0 .4 V lower than the first discharge plateau of Li-B/ FeS_2 cell . In our experiments , the voltage drop in discharge curves includes three parts : ① the voltage drop from the Li-B alloy , ~ 0 .2 V ; ② the voltage drop from the cathode $FeS_2 \rightarrow Fe_{0.96}S$, ~ 0 .4 V ; ③ the voltage drop from concentration polarization . Besides the effects of cathode materials on the discharge curves , the phenomenon often discovered is that because uniform expansion of cathode pellet in discharge test , some area of the Li-B anode is in contact with the electrolyte , but other area is not , which can lead to discharge experiment failure . How to deal with this kind of problem is a very important technical issue .

5　CONCLUSIONS

(1) FeS_2 cathode powder with fine particle size (< 44 μm) needs 2 .5 % Li_2O addition quantity to eliminate the first pulse peak in discharge curves of Li-B/ FeS_2 cells . Roasting the cathode mixture powder at 400 ℃ can lower the addition quantity of Li_2O .

(2) After heating at 700 ℃ , the FeS_2 will decompose to $Fe_{1-x}S$, where $x = 0.024 \sim 0.066$.

(3) Before running-out of anode materials , the voltage drop in the discharge curves of Li-B/ FeS_2 cells includes three parts , the drop 0 .2 V corresponding to the transition from Li discharge to ion Li^+ in Li_7B_6 matrix discharge , voltage drop ~ 0 .4 V corresponding to the transition of FeS_2 discharge to $Fe_{0.96}S$ discharge and the voltage drop corresponding to the concentration polarization .

(4) To increase the quantity of cathode and decrease the experimental temperature can delay and even eliminate the voltage drop ~ 0 .4 V corresponding to the cathode materials . Otherwise , the voltage drop 0 .4 V will accelerate but it will lead to concentration polarization decrease .

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