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Review

# Redox mechanism of FeS<sub>2</sub> in non-aqueous electrolyte lithium and sodium batteries

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Primary Li/FeS<sub>2</sub> batteries have been commercialized and rechargeable Li-alloy/FeS<sub>2</sub> batteries have been succeeded for operation at 375–500 °C by employing LiCl-based molten electrolytes. However, non-aqueous electrolyte rechargeable Li/FeS<sub>2</sub> batteries have not yet been fulfilled due to poor reversibility and rapid capacity fading. Redox mechanism of FeS<sub>2</sub> in non-aqueous electrolytes at ambient temperature is poorly understood and is still debated. In this mini-review, we analyse the experimental observations reported previously and propose a suitable mechanism that can explain all of the phenomena observed from the non-aqueous electrolyte Li/FeS<sub>2</sub> and Na/FeS<sub>2</sub> batteries.

## 1. Introduction

Pyrite (FeS<sub>2</sub>) is an abundant and inexpensive natural material that theoretically stores up to 894 Ah/kg capacity based on the complete conversion of FeS<sub>2</sub> to metallic Fe and alkali metal sulphide (Li<sub>2</sub>S or Na<sub>2</sub>S). Therefore, FeS<sub>2</sub> has long been among the preferred choices for the high capacity cathode material of rechargeable batteries. Primary Li/FeS<sub>2</sub> batteries have been commercialized as early as in 1980s<sup>1</sup>, and rechargeable batteries have been succeeded for applications over a temperature range of 375–500 °C by employing a LiCl-rich molten electrolyte and a Li alloy anode that remains solid over the operating temperature range<sup>2, 3</sup>. Additional investigation has shown that the Li/FeS<sub>2</sub> batteries can be cycled up to 500 times in a moderate temperature range of 90–130 °C by employing a composite polymer electrolyte (CPE)<sup>4–6</sup>. In all these batteries, the final discharge products are determined to be metallic Fe and Li<sub>2</sub>S. For the non-aqueous electrolyte system, however, the redox mechanism of FeS<sub>2</sub> at ambient temperature is poorly understood, and the electrochemical processes of the Li/FeS<sub>2</sub> batteries have been the object of a number of publications<sup>5, 7–11</sup>. In particular, the discharging and charging voltage profiles of the Li/FeS<sub>2</sub> cells reported by different authors varied vastly. There is no suitable redox mechanism that can explain all of the experimental observations from the Li/FeS<sub>2</sub> and Na/FeS<sub>2</sub> batteries. In this mini-review, we analyse the experimental observations reported previously, and speculate about a suitable redox mechanism that can explain all of the experimental observations from the Li/FeS<sub>2</sub> and Na/FeS<sub>2</sub> batteries. Since the FeS<sub>2</sub> undergoes the same electrochemical processes in the Li/FeS<sub>2</sub> and Na/FeS<sub>2</sub> batteries, hereafter the Li/FeS<sub>2</sub> battery is also referred as to the Na/FeS<sub>2</sub> battery.

## 2. Crystal structure and electrochemical characteristics of FeS<sub>2</sub>

### 2.1. Crystallographic structure

Pyrite FeS<sub>2</sub> possesses simple cubic structure with space group Pa3̄. The unit cell consists of a Fe face-centred cubic sublattice, into which the S ions are embedded as shown in Fig. 1a. In the first bonding sphere, the Fe atoms are surrounded by six S nearest atoms, in a distorted octahedral arrangement, and the S atoms bind with three Fe and one other S atom<sup>12</sup>. Mössbauer spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses show that the Fe ions are in a low spin divalent state. Therefore, it is believed that the Fe<sup>2+</sup> and (S–S)<sup>2–</sup> are in closed shell entities with each S bound to one Fe and one other S, and that the electronic state of FeS<sub>2</sub> can be expressed as Fe<sup>2+</sup>(S–S)<sup>2–</sup>.

### 2.2. First discharge of Li/FeS<sub>2</sub> battery

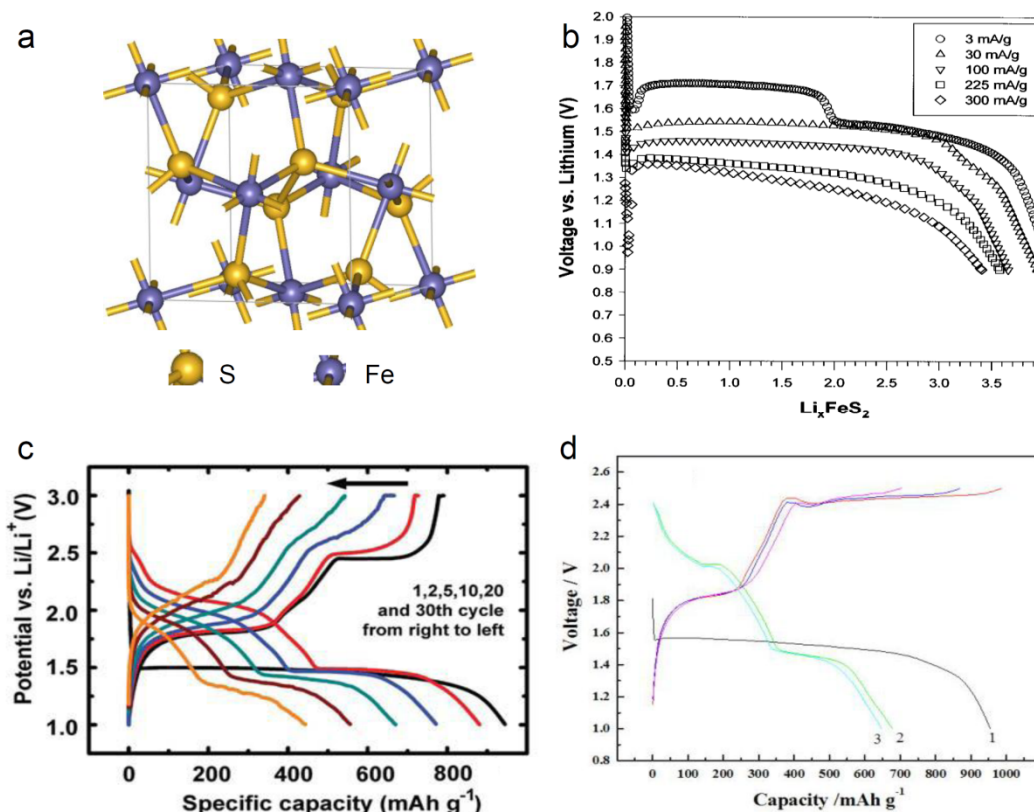
Voltage profile for the first discharge of Li/FeS<sub>2</sub> cells is very reliable and reproducible (see Fig. 1b). Near the thermodynamic equilibrium conditions, the first discharge exhibits two voltage plateaus at 1.7 and 1.5 V, respectively, with equal capacity. Since their voltages are so close, these two voltage plateaus can be distinctly separated only under such conditions as low current rate, high temperature, or small FeS<sub>2</sub> particle size<sup>8, 13</sup>. In most conditions, one can see only a merged voltage plateau at 1.5 V or slightly lower.

### 2.3 Subsequent recharging and cycling

Voltage profiles for the subsequent recharging and cycling become much more complicated and cannot repeat that of the first discharge. The results reported by different authors vary vastly. As indicated in Fig. 1c, the Li/FeS<sub>2</sub> cell can be charged up to 3 V, however, suffers fast capacity fading with cycling in a carbonate-based electrolyte, namely 1.5 M LiPF<sub>6</sub> in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC)<sup>14</sup>. In contrast, the Li/FeS<sub>2</sub> cell cannot be charged beyond 2.4 V in an ether-based electrolyte, namely 1 M LiClO<sub>4</sub> in a 2:1 mixture of dimethoxyethane (DME) and 1,3-dioxolane (DOL), as shown in

Fig. 1d<sup>15</sup>. Instead, the charge voltage remains at ~2.4 V until the charging process is terminated, showing significant redox shuttle and low coulombic efficiency. Other experiments show that voltage profiles of the discharging and charging processes of the Li/FeS<sub>2</sub> cells greatly change with cutoff voltage and current rate

of the charging process no matter what it is a non-aqueous electrolyte cell<sup>8</sup> or a solvent-free CPE cell<sup>16</sup>. It has been consistently reported that the initial FeS<sub>2</sub> structure is hardly recovered once the Li/FeS<sub>2</sub> cells are fully discharged.



**Fig.1** (a) Crystal structure of FeS<sub>2</sub>, (b) voltage profile of the first discharge of Li/FeS<sub>2</sub> cells at different discharging rates, (c) voltage profile of a Li/FeS<sub>2</sub> cell in a 1.5 M LiPF<sub>6</sub> 1:1 EC/DEC electrolyte, and (d) voltage profile of a Li/FeS<sub>2</sub> cell in a 1 M LiClO<sub>4</sub> 2:1 DME/DOL electrolyte. Fig. 1b, 1c, and 1d are reproduced with permission of refs. <sup>13</sup>, <sup>14</sup>, and <sup>15</sup>, respectively.

### 3. Current understanding on the redox processes of FeS<sub>2</sub>

It has been well established that the final discharge products of FeS<sub>2</sub> are metallic Fe and Li<sub>2</sub>S (or Na<sub>2</sub>S for Na/FeS<sub>2</sub> cells) by a number of techniques, including X-ray diffraction (XRD)<sup>8, 11</sup>, XPS<sup>11</sup>, Mössbauer spectrum<sup>11</sup>, X-ray absorption near edge structure (XANES)<sup>9, 11, 17</sup>, and extended X-ray absorption fine structure (EXAFS)<sup>17</sup>. Based on the above established conclusion and two equal capacity voltage plateaus, eq. 1 and eq. 2 have been proposed for the first discharge of a Li/FeS<sub>2</sub> cell:



In which the Li<sub>2</sub>FeS<sub>2</sub> is proposed to be a two-electron reduction intermediate of the FeS<sub>2</sub>. Combination of eq. 1 and eq. 2 leads to eq. 3, which corresponds to a four-electron overall reduction and a theoretical capacity of 894 Ah/kg with respect to the mass of FeS<sub>2</sub>.



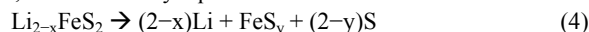
The hypothesis of Li<sub>2</sub>FeS<sub>2</sub> intermediate is based on a Fe-S-Li ternary isothermal phase diagram at 450 °C, which shows that the metastable Li<sub>2</sub>FeS<sub>2</sub> and Li<sub>3</sub>Fe<sub>2</sub>S<sub>4</sub> phases are present near the

thermodynamic equilibrium. The Li<sub>2</sub>FeS<sub>2</sub> was determined to be a layered structure with space group P3m1, consisting of hexagonally-close-packed layers of sulphur with iron and lithium, equally and randomly, filling all of the tetrahedral interstices between two sulphur layers<sup>18</sup>. Since the Li<sub>2</sub>FeS<sub>2</sub> can be formed only near the thermodynamic equilibrium for long time, pure Li<sub>2</sub>FeS<sub>2</sub> phase has never been synthesized at ambient temperature. Following investigations into the redox mechanism of FeS<sub>2</sub> have been overwhelmingly focused on the Li<sub>2</sub>FeS<sub>2</sub> that was synthesised at high temperature with long reaction time. Typically, the synthesis of Li<sub>2</sub>FeS<sub>2</sub> took 3 days at 750 °C for powder form, and a much longer time and higher temperature for single crystal<sup>7</sup>.

Recharging of the discharged Li/FeS<sub>2</sub> cell is assumed to follow the opposite direction of eq. 1 and eq. 2<sup>19</sup>. However, this assumption disagrees with many experimental observations. The recharging process of the Li/FeS<sub>2</sub> cells has been the subject of controversy in a number of publications, which are mainly focused on eq. 1 and the Li<sub>2</sub>FeS<sub>2</sub> intermediate, as summarized below.

The reverse of the discharge reaction shown in eq. 1 was initially considered to be a deintercalation of Li<sup>+</sup> ion from the Li<sub>x</sub>FeS<sub>2</sub>. To verify this, Blandeau et al<sup>7, 20</sup> synthesised a series of

$\text{Li}_x\text{FeS}_2$  with  $x=0.2\sim 2$ , and analysed the Mössbauer and EXAFS spectra of these compounds. They concluded that the deintercalation of  $\text{Li}^+$  ion from  $\text{Li}_x\text{FeS}_2$  consisted of two consecutive steps, (1) the deintercalation of  $\text{Li}^+$  ion from  $\text{Li}_2\text{FeS}_2$  to  $\text{Li}_1\text{FeS}_2$  with an accompanying increase of the Fe valence from  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  and (2) the oxidization of the  $\text{S}^{2-}$  ions to  $(\text{S}-\text{S})^{2-}$  ion for the range from  $\text{Li}_1\text{FeS}_2$  to  $\text{FeS}_2$ , and that the final product was  $\text{Fe}^{3+}\text{S}^{2-}(\text{S}_2)^{2-}_{0.5}$ . According to this mechanism, the initial  $\text{FeS}_2$  can be reversibly recovered, which disagrees with the experimental observations and the fact that Fe in  $\text{FeS}_2$  is in the  $\text{Fe}^{2+}$  valence. More importantly, the system of  $\text{Fe}^{3+}$  ion with  $\text{S}^{2-}$  or  $(\text{S}-\text{S})^{2-}$  ion is thermodynamically instable, the  $\text{Fe}^{3+}$  ion will spontaneously oxidize the  $\text{S}^{2-}$  or  $(\text{S}-\text{S})^{2-}$  ion to longer chain polysulfide anion  $(\text{S}_n)^{2-}$ . For example, Fong et al.<sup>8</sup> observed that the  $\text{Li}/\text{Li}_{2-x}\text{FeS}_2$  cell reached a voltage plateau at 2.45 V when being charged to  $x>0.8$ . Based on the analyses of the *in-situ* XRD and *in-situ* Mössbauer spectroscopy, Fong et al proposed that the  $\text{Li}_{2-x}\text{FeS}_2$  was subject to disproportionation to form nonstoichiometric  $\text{FeS}_y$  ( $y=1.064$ ) and elemental sulphur when  $x$  in  $\text{Li}_{2-x}\text{FeS}_2$  exceeded 0.8, as described by eq. 4.



Therefore, Fong et al.<sup>8</sup> modified the recharging process of  $\text{Li}_{2-x}\text{FeS}_2$  as the reversible deintercalation of  $\text{Li}^+$  ion for  $0<x\leq 0.8$  and irreversible disproportionation of  $\text{Li}_{2-x}\text{FeS}_2$  for  $x>0.8$ . This modification reasonably explains the irreversible structure change of  $\text{FeS}_2$  in the first discharge as well as the loss of polysulphide with repeated cycling<sup>14, 21, 22</sup>.

In addition, voltage profiles of the discharging and charging processes of  $\text{Li}/\text{CPE}/\text{FeS}_2$  cells become very complicated when the cells are cycled in a temperature range of  $70\sim 135^\circ\text{C}$ .<sup>5</sup> In this case, the first (upper) discharge voltage plateau is split into two plateaus, one at about 1.8 V and another at 1.6 V. In order to explain these two voltage plateaus, Peled et al proposed a chemical equilibrium existing between eq. 1 and eq. 2, as

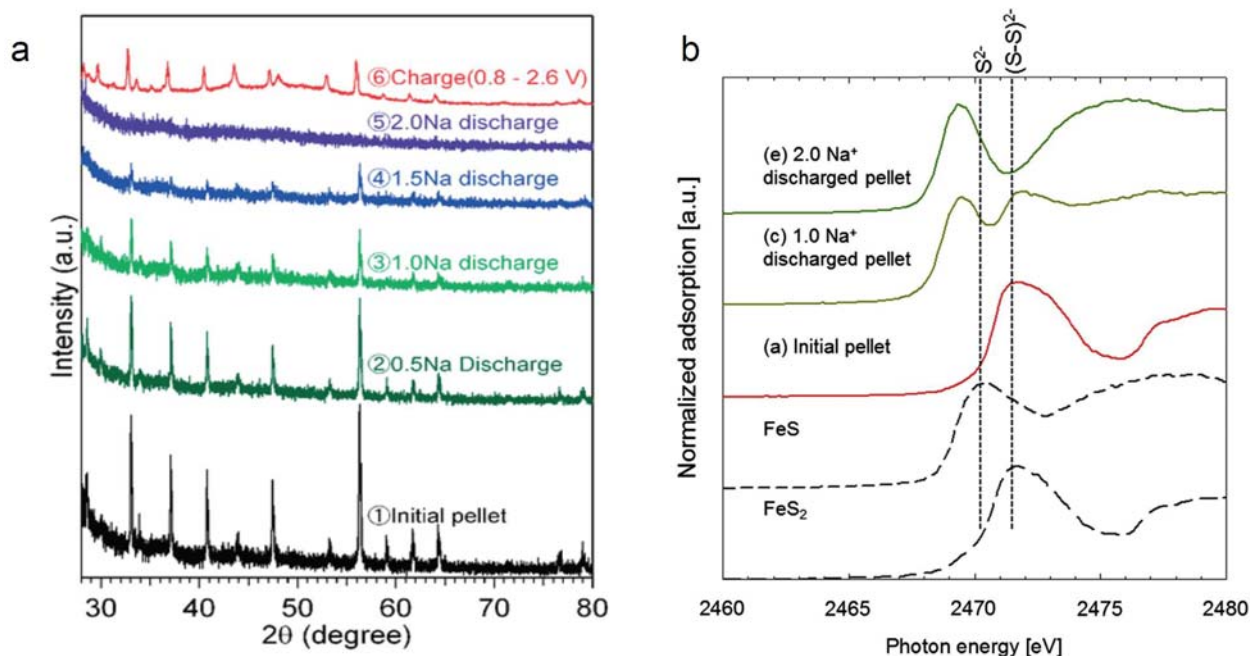
described by eq. 5<sup>4, 5, 17</sup>.



This chemical equilibrium was partially supported by Shao-Horn et al.<sup>13</sup> who observed plate-like  $\text{Li}_2\text{S}$  crystals co-existed with  $\text{Li}_2\text{FeS}_2$  at the end of the upper voltage plateau during the first discharge of the  $\text{Li}/\text{FeS}_2$  cells.

According to the redox processes described above, the lattice parameter of  $\text{FeS}_2$  crystal cell as well as the valence of centre Fe atom must change with the intercalation and deintercalation of  $\text{Li}^+$  ion. Unfortunately, such changes could not be observed experimentally. Firstly, it is shown that during discharge from  $\text{FeS}_2$  to  $\text{Na}_2\text{FeS}_2$  for a  $\text{Na}/\text{FeS}_2$  cell, the XRD peaks of  $\text{FeS}_2$  do not change position, instead, decrease in intensity, as indicated by Fig. 2a<sup>11</sup>. This means that the discharge from  $\text{FeS}_2$  to  $\text{Na}_2\text{FeS}_2$  only reduces the amount of  $\text{FeS}_2$ , but does not change the crystal structure of the  $\text{FeS}_2$ . Secondly, the *in-situ* Fe K-edge EXAFS and XANES analyses reveal that the  $\text{Fe}^{2+}$  valence remains unchanged over entire two-electron reduction (discharge) process of the  $\text{FeS}_2$  in both the  $\text{Li}/\text{FeS}_2$  cell<sup>9</sup> and  $\text{Na}/\text{FeS}_2$  cell<sup>11</sup>. Instead, the sulphur K-edge XANES spectra of the  $\text{FeS}_2$  show that the discharge from  $\text{FeS}_2$  to  $\text{Na}_2\text{FeS}_2$  results in breakage of the  $(\text{S}-\text{S})^{2-}$  bond into  $\text{S}^{2-}$  ions, as indicated in Fig. 2b. Thirdly, the  $\text{Li}_2\text{FeS}_2$  has never been experimentally observed from  $\text{Li}/\text{FeS}_2$  cells by XRD except for the assumption that the formed  $\text{Li}_2\text{FeS}_2$  is amorphous and undetectable by XRD<sup>8</sup>. The above facts reveal that in recharging, eq. 1 is unlikely to be an intercalation-deintercalation process of the  $\text{Li}^+$  ion, instead a breakage-recombination process of the  $(\text{S}-\text{S})^{2-}$  bond.

As summarized above, the current understanding on the redox mechanism of  $\text{FeS}_2$  in non-aqueous electrolyte batteries cannot explain a number of experimental observations, and there is no convincing evidence for the presence of a  $\text{Li}_2\text{FeS}_2$  intermediate. A better understanding of the  $\text{FeS}_2$  redox process is vital for the development of viable  $\text{Li}/\text{FeS}_2$  and  $\text{Na}/\text{FeS}_2$  batteries.



**Fig. 2** *In-situ* spectra of  $\text{FeS}_2$  during the first discharge and recharge. (a) XRD patterns, and (b) S K-edge XANES. Reproduced with permission of ref. <sup>11</sup>.

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## Review

#### 4. Insight into the redox mechanism of FeS<sub>2</sub> in non-aqueous electrolyte

The following are a brief summary for established facts, reported by independent research groups, about the Li/FeS<sub>2</sub> and Na/FeS<sub>2</sub> batteries:

1. Final discharge products are metallic Fe and Li<sub>2</sub>S (or Na<sub>2</sub>S for Na/FeS<sub>2</sub> cell) <sup>5, 8, 9, 11</sup>.

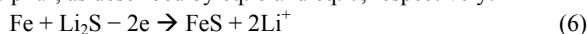
2. FeS<sub>2</sub> structure is irreversibly changed in the first discharge, and crystalline Li<sub>2</sub>FeS<sub>2</sub> has never been observed to form in non-aqueous liquid electrolytes at ambient temperature <sup>8, 9</sup>.

3. There is no change in the Fe<sup>2+</sup> valence except for the breakage and recombination of the (S-S)<sup>2-</sup> bond during electrochemical cycling in the upper voltage plateau region <sup>9, 11</sup>.

4. Cycling leads to progressive loss of polysulphide. In particular, the cell suffers severe redox shuttle at 2.4 V in ether-based electrolytes <sup>10, 15, 23</sup> and poor reversibility in carbonate-based electrolytes <sup>8, 11, 14, 22, 24, 25</sup>.

5. There is a significant loss in the capacity from the 1<sup>st</sup> to 2<sup>nd</sup> discharge, and the first discharge voltage profile cannot be repeated by subsequent cycles <sup>6, 8, 10, 14, 15, 22-24</sup>.

Based on the facts above, recharging of the discharged FeS<sub>2</sub> can be more reasonably described using the following two conversion reactions: (1) the conversion of metallic Fe to FeS and (2) the oxidization of Li<sub>2</sub>S through lithium polysulphide to sulphur, as described by eq. 6 and eq. 7, respectively.



Similar to the non-aqueous liquid electrolyte Li/S batteries <sup>26</sup>, the electrochemical oxidization of Li<sub>2</sub>S (eq. 7) undergoes through a series of lithium polysulphide (Li<sub>2</sub>S<sub>n</sub>, 2 ≤ n ≤ 8) intermediates, which may dissolve into the liquid electrolyte as the n in Li<sub>2</sub>S<sub>n</sub> reaches or exceeds 4. Therefore, the Li/FeS<sub>2</sub> cells suffer from the same problems as occurred in the Li/S batteries, such as the loss of sulphur active material, redox shuttle, and Li corrosion. It was reported that no new crystalline phases could be detected by XRD during cycling of the Li/FeS<sub>2</sub> cells <sup>8, 11</sup>. Therefore, the FeS formed in eq. 6 is believed to be amorphous and embedded within the remaining Li<sub>2</sub>S matrix. Chemical interaction between the FeS and the S<sub>n</sub><sup>2-</sup> anion formed in further charging (eq. 7) benefits the suppression of the dissolved lithium polysulphide from diffusing out of the cathode. An extreme for such chemical interactions is that the FeS and S<sup>-</sup> radical anion (i.e., one of the intermediates of Li<sub>2</sub>S oxidization) are directly combined to form FeS<sub>2</sub>, as suggested by some of the XRD peaks of FeS<sub>2</sub> in Fig. 2a, which was obtained when a fully discharged Na/FeS<sub>2</sub> cell was recharged to 2.6 V <sup>11</sup>. Based on the above analyses, after the first discharge the Li/FeS<sub>2</sub> cells simply become a hybrid of a Li/FeS cell (eq. 6) and a Li/S cell (eq. 7). In charging, metallic Fe is first oxidized to form FeS, and then the remaining Li<sub>2</sub>S is oxidized to produce from insoluble short-chain polysulphides (Li<sub>2</sub>S<sub>n</sub>, n=2 or 3) through soluble long-chain polysulphides (Li<sub>2</sub>S<sub>n</sub>, 4 ≤ n ≤ 8) to

elemental sulphur (S<sub>8</sub>). As usual, the discharging process follows the opposite direction of eq. 7 and eq. 6 in sequence. With the similar principle, we believe that the present mechanism is also applicable to other transition metal monosulphides <sup>27</sup> and polysulphides <sup>28</sup>, when such compounds are used as the cathode material of rechargeable lithium and sodium batteries.

Eq. 7 is well supported by the fact that the Li/FeS<sub>2</sub> cells share many commonalities with the Li/S cells, including the multiple discharge voltage regions, chemical compatibility with liquid electrolyte, and particularly the problems in relation to the dissolution of long-chain lithium polysulphides in the liquid electrolyte. With an increase in the charging cutoff voltage, the charge products of eq. 7 are dominated in turn by insoluble Li<sub>2</sub>S<sub>n</sub> (n=2 or 3), soluble Li<sub>2</sub>S<sub>n</sub> (4 ≤ n ≤ 8), and elemental sulphur (S<sub>8</sub>). Therefore, the charging cutoff voltage greatly affects the cycling performance and reversibility of the Li/FeS<sub>2</sub> cells. The Li/FeS<sub>2</sub> cells can be well reversible only when the charge products of eq. 7 are strictly controlled within the insoluble Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S<sub>3</sub> regions. In particular, polysulphide anions in solution are highly reactive with carbonate solvents <sup>26</sup>. In order to use a carbonate-based electrolyte in the Li/FeS<sub>2</sub> cells, the charging process must be limited within the low voltage (<2.2 V) so as not to form soluble lithium polysulphides (Li<sub>2</sub>S<sub>n</sub>, n ≥ 4). It should be noted that eq. 7 is a multiple-stage reaction, in which the potentials for the conversion between Li<sub>2</sub>S and Li<sub>2</sub>S<sub>2</sub> are very close to those of eq. 6. Therefore, eq. 6 and eq. 7 are more likely to compete with each other, making the voltage profile of Li/FeS<sub>2</sub> cells very complicated. For example, the Li/CPE/FeS<sub>2</sub> cells exhibit up to six distinguishable voltage domains when being cycled at 135 °C between 1.1 V and 2.25 V <sup>7</sup>. In addition, the upper discharge voltage plateau of the Li/FeS<sub>2</sub> cell can be elevated to 2 V or higher when the Li anode is protected from contact with the dissolved lithium polysulphide by a LiPON solid electrolyte <sup>29</sup> or when a solid state electrolyte is used <sup>22</sup>. According to the present understanding, the Li/FeS<sub>2</sub> (and Na/FeS<sub>2</sub>) cells are simply a combination of the Li/FeS cell and Li/S cell. The approaches that have been proven to be effective in improving the conversion-type batteries and Li/S batteries must be applicable to the rechargeable Li/FeS<sub>2</sub> batteries. As an example, Takeuchi et al <sup>25</sup> demonstrated that adding extra Li<sub>2</sub>S into FeS<sub>2</sub> to form a FeS<sub>2</sub>-Li<sub>2</sub>S composite significantly increases the reversible capacity and reversibility of the upper voltage plateau at ~2 V for the Li/FeS<sub>2</sub> cells. Such improvements are attributed to the extra sulphur introduced by the Li<sub>2</sub>S.

#### 5. Conclusions and remarks

In summary, the redox mechanism and final products for the first discharge of the Li/FeS<sub>2</sub> and Na/FeS<sub>2</sub> batteries have been well established. The first discharge consists of two equal capacity steps, first reduction from (S-S)<sup>2-</sup> into S<sup>2-</sup> and then conversion from Fe<sup>2+</sup> into Fe, to form metallic Fe and Li<sub>2</sub>S (or Na<sub>2</sub>S for the Na/FeS<sub>2</sub> cells) as the final products. The subsequent recharging

and cycling are composed of two conversion reactions, one between Fe and  $\text{Fe}^{2+}$  for the lower voltage plateau and the other between  $\text{Li}_2\text{S}$  and lithium polysulphides or elemental sulphur for the upper voltage plateau. Most of the controversies on the  $\text{Li}/\text{FeS}_2$  cells have been focused on the redox mechanism and redox intermediate of the upper voltage plateau. Many experimental results indicate that the metastable  $\text{Li}_2\text{FeS}_2$  intermediate is unlikely to be formed, and that the upper voltage plateaus is attributed to a breakage-recombination process of the  $(\text{S}-\text{S})^{2-}$  bond other than an intercalation-deintercalation process of the  $\text{Li}^+$  ion. After the first discharge, the  $\text{Li}/\text{FeS}_2$  cells convert into a hybrid of the  $\text{Li}/\text{FeS}$  cell and the  $\text{Li}/\text{S}$  cell. Most problems, such as inferior rate capability, poor reversibility and fast capacity fading, with the  $\text{Li}/\text{FeS}_2$  cells are due to the slow conversion kinetics and growth of Fe particles or even Fe dendrites for the  $\text{Li}/\text{FeS}$  cell, and due to the dissolution of long-chain lithium polysulphides and the resultant parasitic reactions for the  $\text{Li}/\text{S}$  cell. The knowledge learned from the conversion-type cells and  $\text{Li}/\text{S}$  cells is very helpful for understanding the performance of the  $\text{Li}/\text{FeS}_2$  (and  $\text{Na}/\text{FeS}_2$ ) cells, and the strategies used for improving the conversion-type cells and  $\text{Li}/\text{S}$  cells must be applicable to these batteries. In comparison with elemental sulphur, the  $\text{FeS}_2$  is much safer (due to high melting point) and competitive in the cost and earth crust distribution. In near future, it could be more feasible to develop the rechargeable  $\text{Li}/\text{FeS}_2$  and  $\text{Na}/\text{FeS}_2$  batteries than the  $\text{Li}/\text{S}$  batteries.

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## Notes and references

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1. D. Linden and T.B. Reddy, Handbook of Batteries, 3rd edition, Chapter 14, McGraw-Hill, 2002.
  2. Z. Tomczuk, M. F. Roche and D. R. Vissers, *J. Electrochem. Soc.*, 1980, **127**, C348–C348.
  3. Z. Tomczuk, B. Tani, N. C. Otto, M. F. Roche and D. R. Vissers, *J. Electrochem. Soc.*, 1982, **129**, 925–931.
  4. E. Peled, D. Golodnitsky, G. Ardel, J. Lang and Y. Lavi, *J. Power Sources*, 1995, **54**, 496–500.
  5. E. Peled, D. Golodnitsky, E. Strauss, J. Lang and Y. Lavi, *Electrochim. Acta*, 1998, **43**, 1593–1599.
  6. E. Strauss, D. Golodnitsky and E. Peled, *Electrochim. Acta*, 2000, **45**, 1519–1525.
  7. R. Brec, E. Prouzet and G. Ouvrard, *J. Power Sources*, 1989, **26**, 325–332.
  8. R. Fong, J. R. Dahn and C. H. W. Jones, *J. Electrochem. Soc.*, 1989, **136**, 3206–3210.
  9. D. A. Totir, I. T. Bae, Y. N. Hu, M. R. Antonio, M. A. Stan and D. A. Scherson, *J. Phys. Chem. B*, 1997, **101**, 9751–9756.
  10. T. B. Kim, J. W. Choi, H. S. Ryu, G. B. Cho, K. W. Kim, J. H. Ahn, K. K. Cho and H. J. Ahn, *J. Power Sources*, 2007, **174**, 1275–1278.
  11. A. Kitajou, J. Yamaguchi, S. Hara and S. Okada, *J. Power Sources*, 2014, **247**, 391–395.
  12. G. Brostigen and A. Kjekshus, *Acta Chem. Scand.*, 1969, **23**, 2186–2188.
  13. Y. Shao-Horn, S. Osmialowski and Q. C. Horn, *J. Electrochem. Soc.*, 2002, **149**, A1499–A1502.

14. S. B. Son, T. A. Yersak, D. M. Piper, S. C. Kim, C. S. Kang, J. S. Cho, S. S. Suh, Y. U. Kim, K. H. Oh and S. H. Lee, *Adv. Energ. Mater.*, 2014, **4**, 1300961.
15. Y. R. Wang, H. T. Liao, J. Wang, X. F. Qian, Y. C. Zhu and S. Q. Cheng, *Int. J. Electrochem. Sci.*, 2013, **8**, 4002–4009.
16. L. A. Montoro, J. M. Rosolen, J. H. Shin and S. Passerini, *Electrochim. Acta*, 2004, **49**, 3419–3427.
17. S. Kostov, M. denBoer, E. Strauss, D. Golodnitsky, S. G. Greenbaum and E. Peled, *J. Power Sources*, 1999, **81–82**, 709–714.
18. R. J. Batchelor, F. W. B. Einstein, C. H. W. Jones, R. Fong and J. R. Dahn, *Phys. Rev. B*, 1988, **37**, 3699–3702.
19. A. Le Mehaute, R. Brec, A. Dugast and J. Rouxel, *Solid State Ionics*, 1981, **3–4**, 185–189.
20. L. Blandeau, G. Ouvrard, Y. Calage, R. Brec and J. Rouxel, *J. Phys. C Solid State*, 1987, **20**, 4271–4281.
21. L. A. Montoro and J. M. Rosolen, *Solid State Ionics*, 2003, **159**, 233–240.
22. T. Evans, D. M. Piper, S. C. Kim, S. S. Han, V. Bhat, K. H. Oh and S. H. Lee, *Adv. Mater.*, 2014, **26**, 7386–7392.
23. T. A. Yersak, H. A. Macpherson, S. C. Kim, V.-D. Le, C. S. Kang, S. B. Son, Y. H. Kim, J. E. Trevey, K. H. Oh, C. Stoldt and S. H. Lee, *Adv. Energ. Mater.*, 2013, **3**, 120–127.
24. J. Liu, Y. Wen, Y. Wang, P. A. van Aken, J. Maier and Y. Yu, *Adv. Mater.*, 2014, **26**, 6025–6030.
25. T. Takeuchi, H. Kageyama, K. Nakanishi, Y. Inada, M. Katayama, T. Ohta, H. Senoh, H. Sakaebe, T. Sakai, K. Tatsumi and H. Kobayashi, *J. Electrochem. Soc.*, 2012, **159**, A75–A84.
26. S. S. Zhang, *J. Power Sources*, 2013, **231**, 153–162.
27. Y. Kim and J. B. Goodenough, *J. Phys. Chem. C*, 2008, **112**, 15060–15064.
28. W. L. Bowden, L. H. Barnette and D. L. Demuth, *J. Electrochem. Soc.*, 1988, **135**, 1–6.
29. V. Pelé, F. Flamary, L. Bourgeois, B. Pecquenard and F. Le Cras, *Electrochem. Commun.*, 2015, **51**, 81–84.