Electrochemical characteristics of room temperature Li/FeS$_2$ batteries with natural pyrite cathode

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Abstract

Electrochemical characteristics of Li/FeS$_2$ batteries having natural pyrite as cathode and liquid electrolytes have been studied at room temperature. The organic electrolytes used were 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in tetra(ethylene glycol) dimethyl ether (TEGDME) or a mixture of TEGDME and 1,3-dioxolane (DOX), and 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The pyrite powder and FeS$_2$ cathode were characterized by SEM, EDS, XRD and charge/discharge cycling. The discharge capacities of Li/FeS$_2$ cells with 1 M LiTFSI dissolved in TEGDME were 772 mAh g^{-1} at the 1st cycle and 313 mAh g^{-1} at the 25th cycle at 0.1C. The cycling performance could be improved by using a mixture of TEGDME and DOX as the electrolyte. It was found that TEGDME contributed to high initial discharge capacity, whereas, DOX contributed to better stabilization of the performance. The first discharge capacities of Li/FeS$_2$ cells showed a decreasing trend with higher current densities (615 and 534 mAh g^{-1}, respectively, at 0.5C and 1.0C). Li/FeS$_2$ cells with the battery grade electrolyte 1 M LiPF$_6$ in EC/DMC had lower initial discharge capacity and cycling capability compared to the TEGDME system. The natural pyrite cathode with 1 M LiTFSI dissolved in a mixture of TEGDME and DOX showed reasonably good first discharge capacity and overall cycling performance, suitable for application in room temperature lithium batteries.
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1. Introduction

The development of compact, light-weight batteries offering high-energy densities are of enormous interest in industry as well as research for applications in miniaturized electronic devices as well as in electric vehicles (EV) and hybrid electric vehicles (HEV). Substantial amount is being invested by advanced nations for the research and development of new battery materials and technology that potentially could increase energy storage and charge/discharge performance, improve durability and reliability and reduce cost. Lithium batteries have gained more attraction in this regard since they provide higher energy density compared to other rechargeable systems [1–3].

In lithium-based commercial rechargeable batteries, the cathodes are made of expensive synthetic compounds such as LiCoO$_2$. There is a growing interest in replacing such cathodes with materials that are easily available, cheaper and providing high energy density when coupled to lithium. Iron disulfide (FeS$_2$) has been projected as one of the best candidate cathode materials, especially for applications in EV/HEVs [4]. Natural FeS$_2$ ore (pyrite) is a non-toxic, "green" material, available in abundance at low cost (~US$ 0.5 kg^{-1}, compared to US$ 30–80 kg^{-1} for lithiated metal oxides). The material cost of the Li/FeS$_2$ battery using a composite polymer electrolyte has been estimated to be about US$ 40 kWh^{-1} (excluding the case), a sixth that of the Li-ion and other Li-polymer electrolyte batteries (~US$ 250 kWh^{-1}) [5]. The theoretical specific energy of the

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Li/FeS$_2$ couple is very high (1273 Wh kg^{-1} based on 4e/FeS$_2$) compared to the Li-ion batteries (580 Wh kg^{-1}) [6]. The other advantages of Li/FeS$_2$ system include the possibility of over-charge protection (based on the fact that FeS$_2$ can be further oxidized) and the cooling of the battery, especially larger EV type batteries, at high discharge rates (because of the large positive entropy change for the discharge of molten LiAl/FeS$_2$ at high temperatures) [4].

The investigations on the utilities of natural pyrite as well as synthetic FeS$_2$ as cathode materials in Li cells started about two decades back [7]. Peled's team has been actively involved in developing FeS$_2$-based cathode materials for use in bipolar Li-polymer batteries for EV applications [4–6,8–10]. They have studied in detail the Li/FeS$_2$ (pyrite) batteries with both composite solid electrolyte (CSE) and composite polymer electrolyte (CPE), which demonstrated high specific energy of 140 Wh kg^{-1} and reversible capacity of 625 mAh g^{-1} at 135 °C [4,6]. The electrochemical behavior of pyrite during the charge/discharge processes in the polymer electrolyte systems used in such batteries was investigated and the major phases that are formed during cell cycling were recognized [9]. More recently, this team has evaluated different types of hybrid polymer electrolytes (HPEs) and gel polymer electrolytes (GPEs) for Li/pyrite battery and compared their performance and obtained specific capacity of the first discharge at 650–1000 mAh g^{-1} and a reversible specific capacity of 250–600 mAh g^{-1} at 70 °C [8]. By using electrochemically deposited thin iron sulfide (which is a mixture of mono- and di-sulfides and non-stoichiometric FeS$_{1+x}$ phases) as cathode in Li/CPE/FeS$_{1+x}$ micro-batteries, good cycle capacity and Faradaic efficiency at 125 °C was reported [10].

Li/FeS$_2$ primary cells containing lithium salts dissolved in organic electrolytes have been commercialized for use in electronic equipments. High-temperature Li/FeS$_2$ rechargeable batteries operating at >120 °C using different combinations of lithium salts and electrolytes have been explored intensively for many years, but are yet to be commercialized. Investigations on room temperature performance of Li/FeS$_2$ cells have been limited and the studies so far carried out have shown inadequate electrochemical characteristics and cycling properties of the cells [8,11,12]. With a view to develop an environment-friendly and economically acceptable cathode material for lithium batteries with good performance at room temperature, we have investigated the properties of Li/pyrite cells with natural pyrite as cathode. The cathode material was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), EDS mapping and electrochemical methods. The effect of organic electrolyte as well as the current rate on the discharge capacity of the cells was studied at room temperature and the results obtained are presented in this paper.

2. Experimental

2.1. Materials

Natural pyrite (FeS$_2$, Chile) was used in this study. Natural pyrite was ball-milled for 6 h and the powder obtained was sieved (400 mesh). Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, Aldrich Chem. Co.) was dried under vacuum at 100 °C for 12 h before use. Tetra(ethylene glycol) dimethyl ether (TEGDME, Aldrich Chem. Co.), 1,3-dioxolane (DOX, Aldrich Chem. Co.) and EC/DMC in 1:1 (v/v) ratio (Merck) were dried over 4 Å molecular sieves before use and verified by Karl-Fischer coulometer (Metrohm) to have moisture content of less than 20 ppm. The liquid electrolyte consisted of 1 M LiTFSI dissolved in a mixture of TEGDME and DOX (in 3:7 or 7:3, v/v ratio) and 1 M LiPF$_6$ dissolved in EC/DMC 1:1 (v/v) ratio (Cheil Industries).

2.2. Preparation of FeS$_2$ cathode

To prepare FeS$_2$ cathode, the active material (natural pyrite, 60 wt.%) was homogeneously mixed with poly(vinylidene fluoride) [PVdF, Aldrich Chem. Co., 15 wt.%] binder, acetylene black (Alfa Aesar, 25 wt.%) conducting agent, and N-methyl-pyrrolidone (NMP, Aldrich). The slurry was spread uniformly upon aluminum foil (current collector) at room temperature using doctor-blade casting method. The composite film was dried at 80 °C for 12 h in an air oven and was cut into disk electrodes (1.1 cm diameter). These electrode disks were dried again in vacuum oven at 80 °C for 24 h and then stored within an argon-filled glove box. The thickness of the resulting composite electrodes ranged from 25 to 30 μm.

2.3. Physical and structural characterization

The pyrite powder and composite cathode were characterized by SEM (JEOL JSM 5600) and X-ray diffraction (XRD, D8 Advance, Bruker AXS, Germany). XRD measurements were performed using the Cu Kα radiation and a graphite monochromator with steps of 0.02° and an integration time of 20 s. Surface image mapping of the composite pyrite cathodes were measured with energy dispersive spectrometer (EDS, INCA Energy, Oxford Instruments).

2.4. Electrochemical characterization

The electrochemical cells studied comprise a lithium metal foil anode, the liquid electrolyte with separator (Celgard®-2400) and natural pyrite cathode. The electrolytes used in the study were (1) 1 M LiTFSI in TEGDME, (2) 1 M LiTFSI in TEGDME/DOX (in 3:7 or 7:3, v/v ratios) and (3) 1 M LiPF$_6$ in EC/DMC (1:1, v/v). The stacked cells were held under pressure inside a coin cell. The electrochemical tests were performed by WBCS 3000 Battery Tester (WonA Tech) at room temperature. The cell was left to electrochemically equilibrate for at least 3 h before the measurement was performed. The charge/discharge performance of Li/FeS$_2$ cell was studied at different current rates of 0.1, 0.5 and 1.0C. The cut-off voltage was set to 1.2 and 2.6 V, respectively. All the experiments in this study were carried out in an argon-filled glove box where H$_2$O content was controlled below 10 ppm.

3. Results and discussion

3.1. Physical and structural characterization of pyrite powder and FeS$_2$ cathode

Natural pyrite after ball milling and sieving to a particle size <40 μm was used as active material in this study. Earlier studies on chemical, structural and electrochemical comparison of natural and synthetic FeS$_2$ in Li/FeS$_2$ cells have shown that the most noticeable differences were the grain sizes, particle distributions and the presence of sulfur-deficient pyrrhotite FeS$_{1.3}$ phase [13]. It was observed that the impure second phases in the natural FeS$_2$ sample were electrochemically inactive and they did not have any significant effects on the discharge of Li/FeS$_2$ cells. Based on the analysis results of the natural and synthetic FeS$_2$ samples, the theoretical specific capacities of the electrodes based on them in lithium cells were calculated and shown to be comparable (850 and 870 mAh g^{-1}, respectively, for natural and synthetic FeS$_2$). Strauss et al. have carried out a comparative characterization of natural pyrite from different sources as cathode material for Li/CPE/FeS$_2$ batteries [9]. The study resulted in the experimental determination that, in spite of the varied extent of contamination in pyrites from different sources, the cells with FeS$_2$-composite cathodes show similar electrochemical behavior and performance characteristics, such as first-cycle utilization, capacity loss and Faradaic efficiency. The above experimental results were encouraging us for selecting the natural pyrite as cathode material, without any further chemical treatments. Moreover, the cost of synthetic FeS$_2$ is very high compared to the natural ore.

The SEM micrographs of as-received and ball-milled natural pyrite powders are shown in Fig. 1(a and b), respectively. The as-received sample (from Chile source) shows the presence of particles of different sizes, with a significant contribution of larger particles of size >10 μm. The sharp edges observed of the larger particles have resulted from the mechanical grinding and powdering of the sample. However, the FeS$_2$ particles did not show strong dimensional anisotropy. As a result of ball milling, the larger particles are broken down and a better uniformity in particle size distribution is achieved (Fig. 1(b)). It has been reported that a uniform particle size distribution leads to good thermal stability of pyrite [9]. It was also observed that a significant amount of relatively small pyrite particles are formed after ball milling which have a tendency to agglomerate together and form larger masses. In the present work, a 6-h ball milling was found to provide better uniformity in particle size distribution for the pyrite sample.

The XRD patterns of natural pyrite powder and the prepared FeS$_2$ cathode are presented in Fig. 2(a and b) respectively. The natural pyrite sample appeared to be phase pure, and the XRD pattern shown in Fig. 2(a) has been indexed to represent the cubic pyrite (FeS$_2$) phase (JCPDS card no. 71-0053). There were no significant levels of impurities in the sample. The XRD pattern of FeS$_2$ composite cathode shows the material to be mostly pyrite, with only trace amounts of FeS (marcassite). The significant reduction of the peak intensity at $2\theta = 56°$, is possibly due to the phase change occurring in the sample at the time of high energy
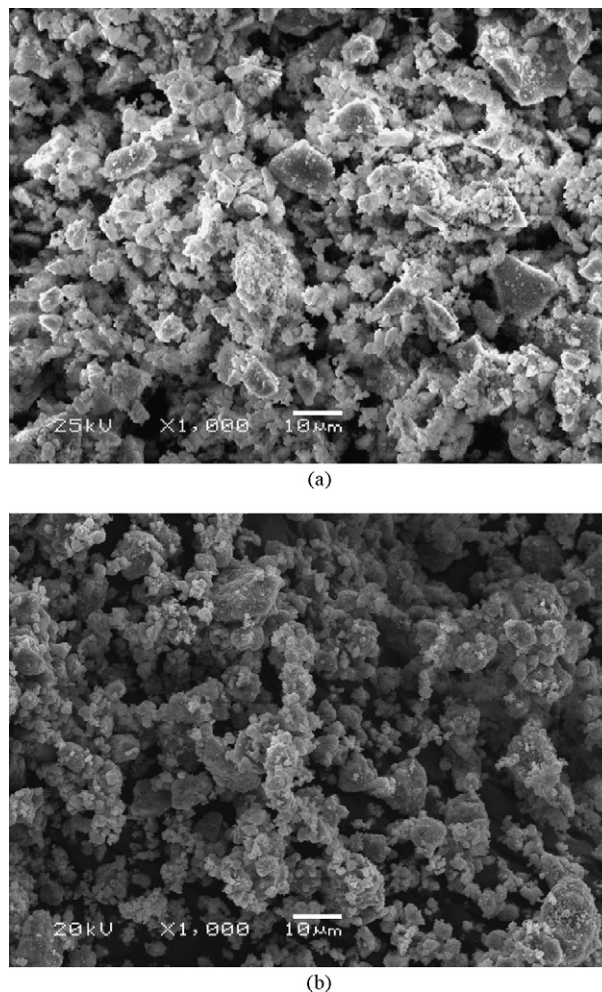

(a)

(b)

Fig. 1. SEM micrographs of natural pyrite powder (a) before ball milling and (b) after ball milling.

ball milling carried out for the preparation of the composite cathode. The morphology of the composite cathode prepared with the ball-milled pyrite is shown in Fig. 3. The pyrite has got dispersed well in the mixture and the size of the particles ranged from submicron to about 4 μm. EDS mapping of the FeS$_2$ cathode was carried out utilizing local X-ray emission of Fe, S, C and F and is shown in Fig. 4. It shows the uniformly dispersed FeS$_2$ particles along with a homogenous distribution of binder (PVDF—detected by fluorine) and conducting agent (carbon black).

3.2. Electrochemical characterization of Li/FeS$_2$ cells

Cyclic voltammetry was carried out to determine the active voltage range for FeS$_2$ electrode at room temperature. Fig. 5 shows the voltammogramms obtained for the first, second and fifth cycles for the Li/pyrite cell with 1 M LiTFSI in TEGDME. For the first cycle, a single reduction peak was seen at 1.3 V and two oxidation peaks at 1.8 and 2.5 V. There is a slight change in the position of the peaks from the second cycle onwards. An additional reduction peak appears at 2.0 V. This indicates the change in lithium/FeS$_2$ reactions between the first and con-
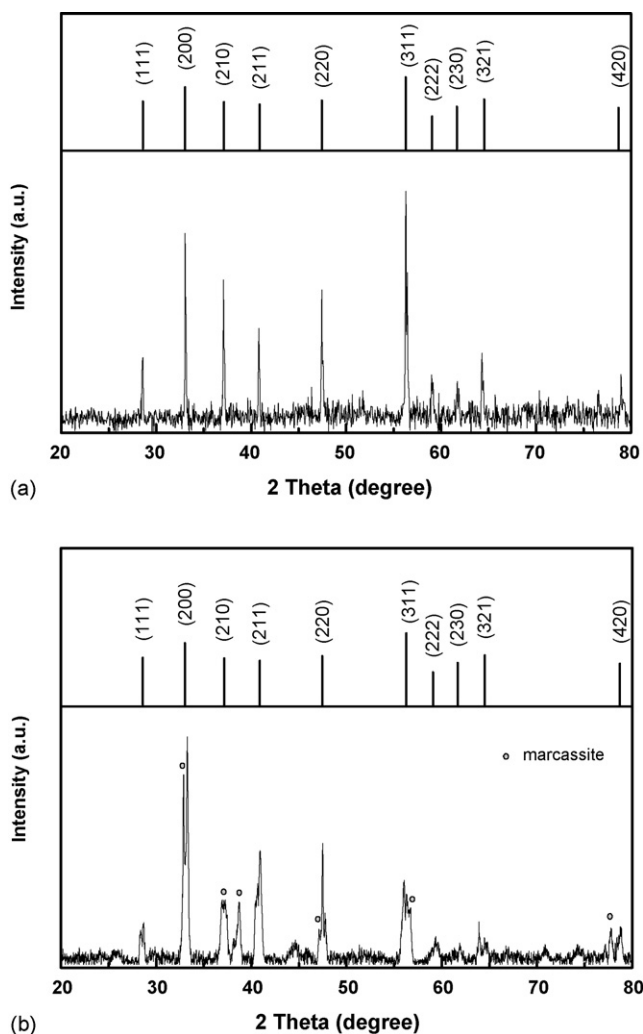
Fig. 2. X-ray diffraction patterns of (a) natural pyrite powder and (b) composite FeS$_2$ cathode.
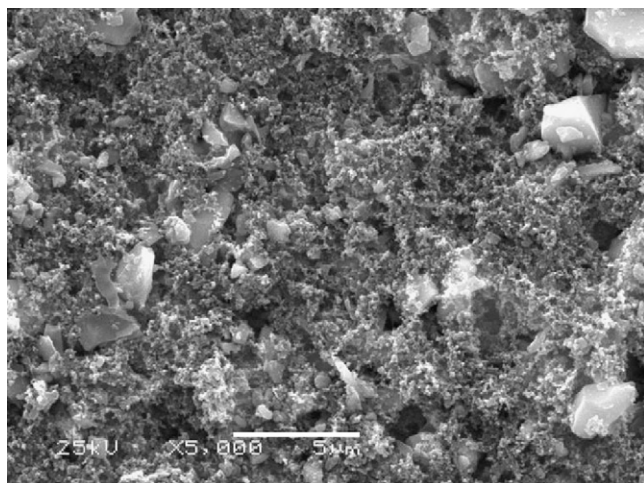

Fig. 3. SEM micrograph of composite natural pyrite cathode.

sequent cycles, which was also observed in discharge curves (Fig. 6, discussed later). As cycle number increased, the oxidation and reduction voltages remained unchanged, indicating better reversibility for the system. The redox current reduced slightly with cycling initially; however, became stable after the first few cycles. Fig. 5 demonstrated that the natural pyrite cathode cycled reversibly at room temperature after a few initial cycles.

The discharge capacity is one of the important performance parameters for rechargeable batteries. Li/pyrite cells have shown good promise as a cathode material for lithium batteries exhibiting high discharge capacities at temperatures >70 °C [4,6,8]. However, the room temperature discharge capacity and cycleability of Li/FeS$_2$ cell has not given encouraging results so far. With Li/tetraglyme-based HPE/FeS$_2$ cells, an initial discharge capacity of 250 mAh g^{-1} was obtained and a degradation rate of 2.1% per cycle over 20 cycles at RT [8]. Employing a gelatin/dimethylsulfoxide (DMSO) treated natural pyrite cathode in Li battery with 1 M LiPF$_6$/EC/DMC electrolyte, an initial discharge capacity 586 mAh g^{-1} was achieved and after 15 cycles, it was 279 mAh g^{-1} [11]. Fig. 6 represents the discharge profile of Li/FeS$_2$ cell in the present study using 1 M LiTFSI dissolved in TEGDME at room temperature during cycle numbers 1, 2, 5, 15 and 25. The open circuit voltage (OCV) of Li/FeS$_2$ cell was 2.7 V. The profile of discharge curve seems to be typical of FeS$_2$ electrodes. A sharp voltage drop to a plateau at 1.5 V occurred during the first discharge. Similar high initial OCV and discharge pattern have been reported for Li/FeS$_2$ cells with LiPF$_6$/EC/DMC [11] and Li/CPE or GPE/pyrite batteries [5,8]. This large voltage variation before the onset of the plateau is attributed to the ohmic potential drop with lithium insertion and a rise of the Fermi level with respect to the conduction band of pyrite. The slope of the first discharge curve is very pronounced, and this is because the cathode is made up of relatively small (∼10 μm) pyrite particles which have high surface area and hence increased sensitivity to the environment. The first discharge at ∼1.5 V for Li/FeS$_2$ cells has been reported by many researchers [8,11–13]. For pyrite electrodes, it has been known that Fe, Li$_2$S, Li$_2$FeS$_2$, FeS or polysulfide may be formed during the first discharge [6,13,14]. The first discharge plateau is associated with the formation of Fe, Li$_2$S and Li-rich phases depending on the quantity of lithium transfer per FeS$_2$. The second discharge curve onwards differs from the first indicating a change in the initial mechanism of pyrite reduction. In addition to the discharge plateau at 1.5 V, an additional plateau appears at ∼2.0 V. It is generally accepted that lithium and FeS$_2$ react in two steps: (1) lithium ions inserting into FeS$_2$ to form an intermediate product, Li$_x$FeS$_2$ (0.5 < x < 0.8), at ∼1.7 V; (2) lithium further reacts with Li$_x$FeS$_2$ to form Li$_2$S and Fe at ∼1.5 V. The second plateau at higher voltages would probably be associated with S oxidation (S^{2-}/S^0 or S^{2-}/S$_2^{2-}$) [11]. It was also reported that the two-step reaction at 1.7 and 1.5 V gradually transformed to one-step reaction at 1.5 V as current density significantly increased, or the two steps in the pyrite reduction proceed simultaneously at room temperature. Ardel et al. has reported the first discharge of Li/FeS$_2$ cells at room temperature with a single plateau at 1.5 V, but
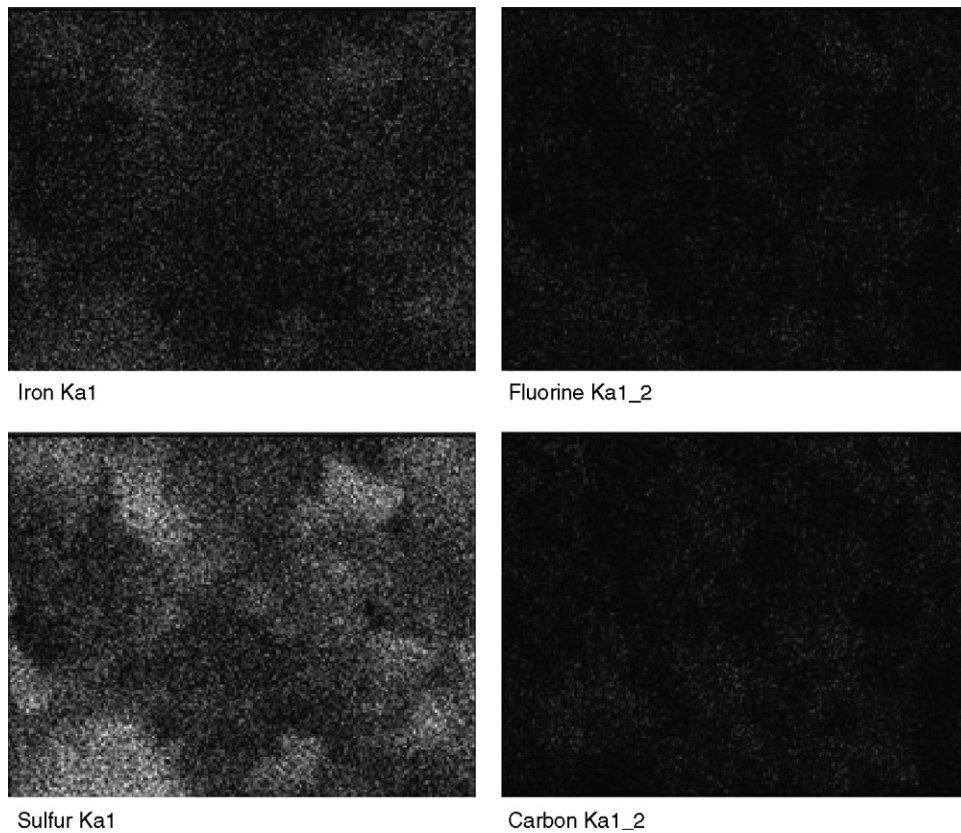
Fig. 4. EDS mapping of composite natural pyrite cathode.

two plateaus were observed at 70 °C even on first discharge [8].

The discharge capacity of FeS_2 electrode with TEGDME-based electrolyte was 772 mAh g^{-1} at first cycle. In this study, the charge/discharge cycling was carried out between 2.6 and 1.2 V with current density of 0.1C. Under these conditions, the lithium concentration transferred to the pyrite cathode reaches about 3.45e/FeS_2. The first discharge capacity at room temperature obtained in our study is higher than what has been earlier reported: 586 mAh g^{-1} by Montoro and Rosolen for Li/FeS_2

cell [11]. They have treated pyrite cathode with gelatin/DMSO, whereas we have used untreated natural pyrite as cathode. As pointed out by earlier workers, specific capacity of the electrode is highly dependent on the particle size of the active material [15]. The higher initial discharge capacity obtained in the present study could be due to the small submicron particle size of pyrite in the cathode which provides higher surface area for active material utilization and promotes faster lithium ion intercalation–deintercalation process. The discharge capacity is found to decrease with the cycle number, with a drastic decrease
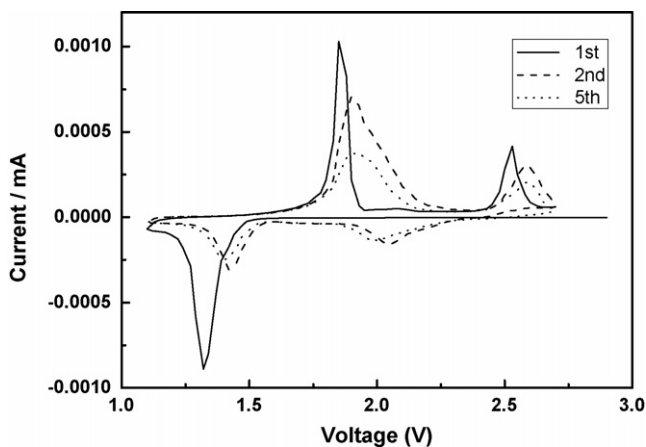

Fig. 5. Cyclic voltammograms of Li/FeS_2 cell at room temperature. The potential sweep rate is 0.1 mV s^{-1} and the voltage range is between 2.8 and 1.1 V.
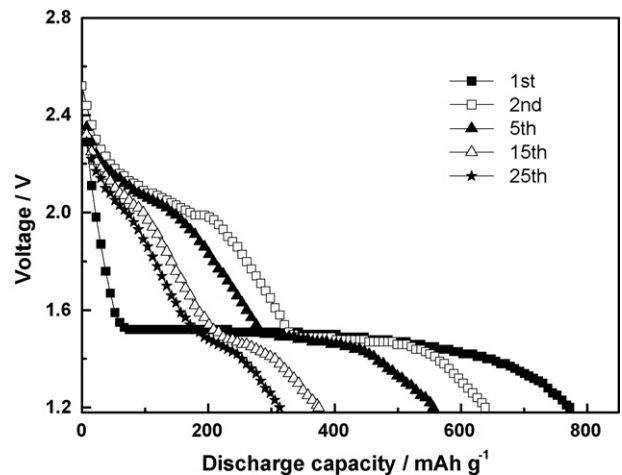

Fig. 6. Discharge curves of Li/FeS_2 cell with 1 M LiTFSI dissolved in TEGDME at room temperature.
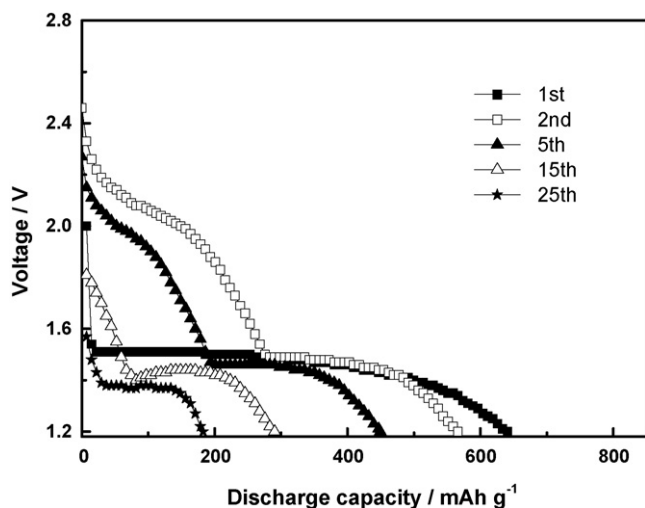
Fig. 7. Discharge curves of Li/FeS$_2$ cell with 1 M LiPF$_6$ dissolved in EC/DMC (1:1, v/v) at room temperature.

Fig. 8. Cycling performance of Li/FeS$_2$ cells using various electrolytes at room temperature.

of 17% between the first and second cycle. The proportions of the different product-rich phases formed from the second discharge onwards depend on the lithium effectively transferred in the first discharge. After 25 cycles, the discharge capacity was 313 mAh g^{-1}, which is about 40.5% of the initial discharge capacity. Although this value does not meet the requirement of 80% capacity retention after repeated cycling, the advantage for the system is that it provides higher discharge capacity even after 25 cycles, compared to the values of other room temperature rechargeable batteries. A similar decrease in discharge capacity was observed for Li/FeS$_2$ system where the first discharge capacity of 586 mAh g^{-1} got reduced to 279 mAh g^{-1} after 15 cycles (47.6% of initial value, compared to 49.2% of initial value for our system after 15 cycles) [11].

In order to evaluate the performance of natural pyrite based cathode for the electrolyte system generally used in commercial lithium batteries, we have studied the discharge profile of Li/FeS$_2$ cells with 1 M LiPF$_6$ dissolved in EC/DMC (1:1, v/v) at room temperature. Fig. 7 shows the discharge curves for Li/FeS$_2$ cell with this electrolyte. For the first discharge, only a single plateau is observed at 1.5 V as in the case of TEGDME system. However, as the cycle number increases, the plateau is shifted to lower voltages, especially after the fifth cycle. Compared with the discharge curves using TEGDME-based electrolyte shown in Fig. 6, the plateau at 2.0 V region disappeared relatively quickly when using EC/DMC. Overall comparison of Figs. 6 and 7 shows that the carbonate type electrolyte has operation voltage lower than ether type electrolyte and the mechanism of lithium/FeS$_2$
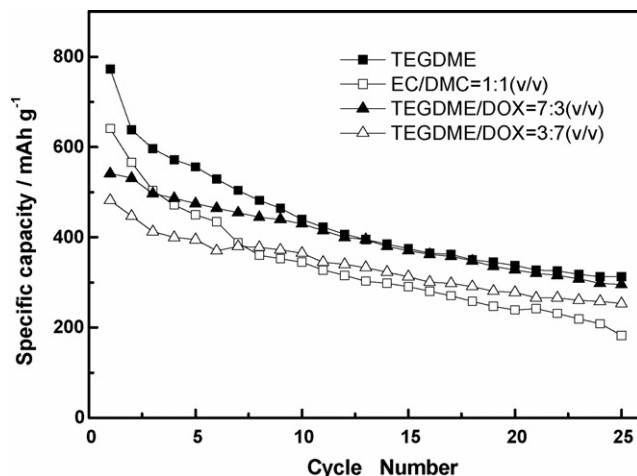
reactions is also different in the two systems. The first discharge capacity for the carbonate electrolyte system was 640 mAh g^{-1} (corresponding to 2.9e/FeS$_2$), lower than that of ether type electrolyte. The discharge capacity decreased with cycle number and was 182 mAh g^{-1} after 25 cycles.

The retention of specific capacity over repeated cycling is one of the important properties required for rechargeable batteries. Fig. 8 compares the specific capacities for discharge performance of Li/FeS$_2$ cells up to 25 cycles at room temperature with the various electrolytes studied here. A comparison of the percentage capacity fading per cycle for the different systems is presented in Table 1. A Li/FeS$_2$ cell with TEGDME shows the highest discharge capacity. However, a continuous decrease in specific capacity is observed during cycling. The capacity fading is maximum between the 1st and 2nd cycle, becomes reasonable during the 10–25 cycles. Ardel et al. has reported the first discharge capacity at room temperature of Li/hybrid polymer electrolyte/FeS$_2$ cell to be 250 mAh g^{-1}, which decreased on cycling and after 25 cycles the capacity loss corresponded to 2.9% per cycle [8]. With natural pyrite cathode and LiTFSI in TEGDME, we obtained initial discharge capacity more than three times with a comparable capacity loss of 2.5% per cycle. It is known that cyclic solvents are better for stabilizing the surface of Li metal by deposition of protective layer that comes from a ring-opening reaction [16,17]. This leads to improved cycling performance of the batteries as a whole. DOX is a common cyclic solvent, freely miscible with TEGDME and hence with a view to improve the cycle performance of the cells, two compositions with TEGDME/DOX in 7:3 and 3:7 (v/v) ratios were studied.

Table 1
The capacity loss (% per cycle) of Li/pyrite cells for various composition of electrolytes at room temperature

Composition of electrolytes	Capacity loss (% per cycle)			
	1st–25th	1st–2nd	2nd–10th	10th–25th
1 M LiTFSI in TEGDME	2.5	17.1	3.9	1.9
1 M LiTFSI in TEGDME:DOX (7:3,v/v)	1.9	2.0	2.4	2.1
1 M LiTFSI in TEGDME:DOX (3:7,v/v)	2.0	7.3	2.3	2.0
1 M LiPF$_6$ in EC:DMC (1:1,v/v)	3.0	11.6	4.9	3.1

From Fig. 8, it can be observed that for TEGDME/DOX (7:3), the initial discharge capacity got reduced to 542 mAh g^{-1}, however, the cycle performance was much better compared to TEGDME system. From Table 1 it can be seen that this electrolyte gives a capacity fading of 1.9% per cycle. After 10 cycles, the curve for this system overlaps the one for TEGDME and the cycle performance of both is similar. For TEGDME/DOX (3:7), the initial discharge capacity was still lower, 482 mAh g^{-1}, but with a comparable capacity loss of 2.0% per cycle. For both systems with DOX as one of the electrolyte components, the capacity fading in the initial cycles was far less compared to the system without DOX, or in other words, DOX contributes to a faster stabilization of the discharge performance of the battery. Generally, it is better to use a mixed solvent consisting of an ether type and cyclic type rather than individually for higher capacity and cycle performance. DOX decreases the viscosity of the electrolyte mixture with TEGDME, favoring the easy transport of lithium ions. The choice of appropriate electrolyte solution is an important factor to be considered for getting high discharge capacities and improved cycling properties for Li/FeS$_2$ cells.

Li/FeS$_2$ cell with 1 M LiPF$_6$ in EC/DMC (1:1, v/v) has an initial discharge capacity higher than the TEGDME/DOX systems; however, the capacity is continuously fading till 25 cycles. After about seven cycles, this system showed the lowest capacity, with retention of only 28.4% of its initial capacity at the 25th cycle. From Table 1 it can be seen that 1 M LiTFSI in TEGDME/DOX (7:3, v/v) electrolyte composition provides the best cycle performance for Li/FeS$_2$ with a capacity fading of 1.9% per cycle. It can be also observed that the capacity fading for this system remained the same through 25 cycles indicating a better reversible performance of the battery. TEGDME/DOX (3:7, v/v) also showed low capacity fading, except for a high loss during the second cycle. Further optimization of TEGDME/DOX ratio could probably lead to a higher initial capacity and cycle performance compared to the ratios investigated here.

The discharge capacities of Li/FeS$_2$ cells with 1 M LiTFSI in TEGDME as a function of current density at room temperature are shown in Fi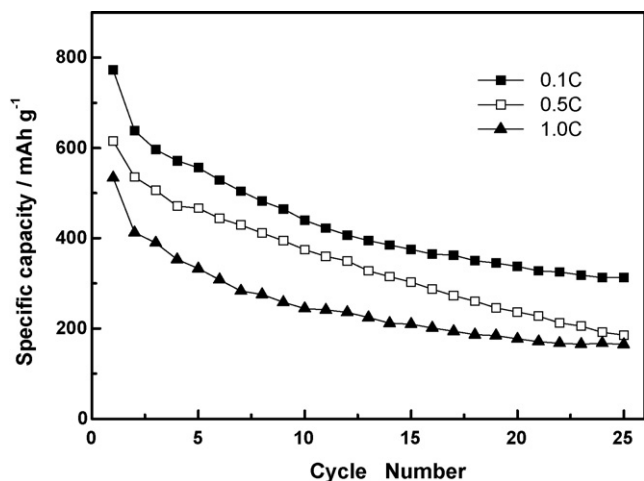g. 9. The charge/discharge cycling was carried out between 2.6 and 1.2 V. The first discharge capacities of Li/FeS$_2$ cell at current densities of 0.1C, 0.5C and 1.0C were 772, 615 and 534 mAh g^{-1}, respectively. The capacities faded with cycle number almost in the same pattern for all the three current densities, i.e. high fading during the initial cycles followed by a stabilization after about 15 cycles. It can be observed that even for the high current density of 1.0C, a discharge capacity of 197 mAh g^{-1} is obtained after 25 cycles, corresponding to 36.5% of initial capacity. A good rate capability is shown by the room temperature Li/pyrite cell studied in this work, giving scope for further optimization of the systems for possible applications in high energy density rechargeable batteries.

4. Conclusion

Natural pyrite was used as a cathode material for Li/FeS$_2$ cells with 1 M lithium LiTFSI in TEGDME or a mixture of TEGDME and DOX, and 1 M LiPF$_6$ in a mixture of EC and DMC, and the electrochemical characteristics were investigated at room temperature. Cyclic voltammetry showed reversibility of the cells after a few initial cycles. The discharge capacities of Li/FeS$_2$ cell at 0.1C current density were 772 and 313 mAh g^{-1} at 1st and 25th cycles respectively at room temperature for 1 M LiTFSI in TEGDME. When a mixture of TEGDME and DOX was used as the electrolyte, the initial discharge capacity was slightly reduced, however, the cycle performance got improved substantially. It was found that TEGDME contributed to high initial discharge capacity, whereas, DOX contributed to better stabilization of the performance. Although discharge capacities were decreased at 0.5 and 1.0 °C compared to the values at 0.1 °C, the cells exhibited good rate capability, indicating its suitability for applications in EV/HEVs. The discharge capacity as well as the cycle performance of Li/FeS$_2$ with 1 M LiPF$_6$ in EC/DMC was lower compared to that in TEGDME based electrolyte. This shows that TEGDME based electrolyte is better suited for performance of Li/FeS$_2$ cells at room temperature compared to EC/DMC. This study has shown natural pyrite to be a promising cathode material for high energy density batteries.

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Fig. 9. Cycling performance of Li/FeS$_2$ cells as a function of current density with 1 M LiTFSI dissolved in TEGDME at room temperature.

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