Li-S Batteries with Li2S Cathodes and Si/C Anodes

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Lithium-sulfur (Li-S) batteries promise improved capacities over lithium ion batteries. While currently mostly metallic lithium anodes are used, the use of silicon-anodes might offer better safety and durability. However, in a lithium-sulfur-Silicon (Li-S-Si) battery, lithium must be introduced either on the anode or on the cathode in form of Li2S. In this study, we have prepared Li2S cathodes in combination with Si anodes (i.e., Si/Li2S full-cells) to investigate both the processes during initial charging/activation of Li2S cathodes and the effect of Li2S cathode activation on the cycling performance of Si/Li2S full-cells. We observed that the initial activation requires a substantially higher charging potential than for the subsequent cycles. In situ XRD analysis of the cathode during the first cycle clearly indicates the gradual transformation of Li2S to polysulfides and finally to crystalline sulfur, i.e., even large Li2S particles (∼20 μm) can be charged completely. The result is further confirmed by ex-situ SEM/EDS analysis, which revealed the formation of large sheets of sulfur at the cathode/separator interface. Similar cycling performance of Si/Li2S full-cells is observed at both 0.1 C and 1 C rates, a clear advantage over Li/Li2S cells, which suffer from severe dendrite formation at 1 C in the case of high Li2S loadings.

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High capacity energy storage systems are needed for various applications ranging from portable electronic devices to automotive applications. For the latter, a safe onboard energy storage system that can provide sufficient driving range is needed. However, the specific energy of current intercalation based lithium ion batteries (∼250–280 Wh/kgcell) substantially limits the driving range compared to that of conventional fuel vehicles1,2 so that batteries offering higher specific energy are required.

Lithium-air (Li2O2)3 and lithium-sulfur (Li-S)4 batteries are among the most widely explored so-called post-lithium ion technologies, for which the lithium ions in the cathode react with either oxygen or sulfur during discharge, resulting in Li2O2 or Li2S discharge product, respectively. Considering the high theoretical specific energy of these post-lithium ion cathodes on the active materials level (viz., ∼3.5 kWh/kgLi2O2 for Li2O2 and ∼2.5 kWh/kgLi2S for Li2S), they are very promising for use in electric vehicles, even though the specific energy gains over lithium ion batteries if compared on the battery system level are substantially lower.6 However, there are still several major issues to be resolved. In the case of Li2O2 batteries, these include the poor charge/discharge reversibility7,8 as well as the poor stability of electrolytes9–11 and of the catalyst support.12 Similarly, Li-S batteries are still plagued by an irreversible loss of active sulfur species, by polysulfide shuttling, and by the continuous electrolyte consumption at the lithium electrode.13,14 Nevertheless, Li-S battery performance/durability has improved significantly over the last few years, mainly by optimizing composite cathodes prepared of sulfur and carbon nanostructures,15 carbon fibers,16 and metal oxides like MnO2 and titanium sub-oxides17,18 as well as by optimizing electrolytes.9,28 With these improvements, Li-S half-cells have reached reversible capacities of >800 mAh/gS after several hundreds of cycles.21

Studies in the field of Li-S batteries have mostly been demonstrated by using metallic lithium as anode, which typically is not used in commercial rechargeable batteries with liquid electrolytes because of safety issues.22 Alternatives to the metallic lithium anode have been widely investigated during the last three decades, focusing mainly on carbon, silicon, and tin.22 Among these, graphite is widely used as anode material in current Li-ion batteries, but it has a relatively low specific capacity (∼372 mAh/gC)22 and is thus not suitable in combination with high capacity cathodes such as sulfur. In contrast, Si offers a high specific capacity (3580 mAh/gS) for the electrochemically reversible Li2Si, but due to its large volume expansion during charging, it suffers from both mechanical degradation and continuous electrolyte consumption due to the instability of the SEI (solid electrolyte interface) on the expanding/contracting silicon surface during charge/discharge. The latter can be partially mitigated by using nanostructured Si (nanowires, nanotubes, nanoparticles, etc.)24,25

One approach to use silicon anodes instead of metallic lithium is to use Li2S (lithium sulfide) rather than S cathodes.26–28 Unfortunately, there are very few studies on full-cells with Li2S cathodes and high capacity Si or Sn anodes. In one study, Li2S/C composites were prepared by milling commercially available Li2S with carbon and testing it in a full cell with a Sn/C composite anode using a polymer electrolyte.28 Another frequently employed approach to prepare a full-cell with a Si anode and a S cathode is through electrochemical pre-lithiation of the Si anode prior to full-cell assembly with a S cathode, as demonstrated by Elazari et al.29 On the other hand, Lui et al. pre-lithiated silicon nanowire electrodes by physically contacting them with metallic lithium and subsequently assembling them into full-cells using S cathodes.30 More recently, Brückner et al. pre-lithiated Si-coated carbon and cycled it against a S cathode with a remaining capacity of ∼400 mAh/gS after >1000 cycles.31

In the present study, we have demonstrated full-cell cycling of a Li2S cathode coupled with a Si/C anode, examining the effect of the initial Li2S cathode activation process and comparing full-cell performance with that of Li2S half-cells (i.e., using a metallic lithium anode). In situ XRD and post-mortem SEM/EDX in combination with three-electrode measurements are used to elucidate the Li2S activation process.

Experimental

Preparation & characterization of Li2S cathodes.— Commercially available Li2S powder (Sigma Aldrich) was used as-received to prepare Li2S cathodes. The Li2S particle size ranged from few hundreds of nanometers to more than 20 micrometer, as shown by the SEM image in Fig. 1a; particle size analysis by laser scattering (not shown) indicated a median diameter of ∼10 μm (volume-averaged distribution).

The ink for the electrode coating was prepared by mechanically mixing the Li2S powder with commercial Vulcan XC72 carbon (∼30 nm primary particles and ∼200–300 nm primary agglomerates) using a mortar and pestle, followed by dispersion in a solution of

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N-Methyl-2-pyrrolidone (NMP) with dissolved polyvinylidenefluoride (PVDF) for two hours using a high speed magnetic stirrer. The solids content of the ink was approximately 150 mg (Li2S+C+PVDF) per milliliter of NMP, with a solids composition of 60%wt Li2S, 30%wt C, and 10%wt PVDF. The ink was coated onto an 18 μm thick aluminum foil using a 300 μm gap doctor blade. Because of the high reactivity of Li2S with moisture, all the processing steps were carried out inside an Ar-filled glove box (MBRAUN; 1 ppm O2 & 1 ppm H2O). After drying inside the glove box, 10 mm diameter electrodes were punched out and further dried at 80 °C under dynamic vacuum in a Buchi oven for 2 hours. For all the measurements, the Li2S loading in the cathode was maintained at 3580 mAh/gSi,32,33 372 mAh/ggraphite, and 150 mAh/gcarbon-black,34 the theoretical areal capacity of the composite anode. The higher capacity observed in the first lithiation is attributed to SEI formation on the Si surface. The potential profile of the subsequent lithiation cycles is different from the first one, reflecting the typical lithiation profile of amorphized silicon.33 As shown in Figure 2b, the 2nd cycle lithiation/delithiation capacities for these Si/graphite composite anodes is nearly independent of rate between C/18 and C/4.5. Overall, from these results it can be concluded that the reversible capacity of the Si anodes in our study is 1.8 mAh/cm2 (within the first four cycles after the initial formation) and does not change significantly within the measured range of C-rates.

**Results and Discussion**

Commericially available Li2S powder with particle size up to 20 μm (Figure 1a) was used to prepare the cathode electrodes. Since the ink for the cathode was prepared by stirring, i.e., without exposing to strong shear forces during mixing, one would expect a similar Li2S particle size distribution in the cathode. This is indeed the case, as illustrated by the electrode surface morphology shown in Figure 1b, where large particles are ascribed to non-fractured Li2S particles.

**Li/Si half-cell characterization**.— Figure 2a shows the initial five charge/discharge cycles of the Si anode in a Li/Si half-cell at a rate of C/4.5 (referenced to the theoretical Si/C anode areal capacity of 2.1 mAh/cm2, and corresponding to a geometric current density of 0.46 mA/cm2). It can be observed that the very first lithiation capacity (red dashed line in Fig. 2a) reaches the calculated theoretical capacity (see Experimental section), following a potential profile which is characteristic of crystalline silicon.31 After the first lithiation and delithiation cycle, the specific lithiation and delithiation capacity decreases to a constant value of ≈1.8 mAh/cm2, corresponding to ≈85% of the theoretical areal capacity of the composite anode. The higher capacity observed in the first lithiation is attributed to SEI formation on the Si surface. The potential profile of the subsequent lithiation cycles is different from the first one, reflecting the typical lithiation profile of amorphized silicon.33 As shown in Figure 2b, the 2nd cycle lithiation/delithiation capacities for these Si/graphite composite anodes is nearly independent of rate between C/18 and C/4.5. Overall, from these results it can be concluded that the reversible capacity of the Si anodes in our study is 1.8 mAh/cm2 (within the first four cycles after the initial formation) and does not change significantly within the measured range of C-rates.

**Activation of Li2S in Li/Li2S and Si/Li2S cells**.— Similar to the initial high-potential activation required during charging of Li2O2 pre-filled cathodes in the case of Li2O2 batteries,36 we found that the initial charging of Li2S cathodes also requires activation at higher potentials. This observation was reported also by Yang et al.26 who showed that a 1 V overpotential is required during the first charge of a Li/Li2S half-cell in comparison to charging a discharged Li/S cell, which they ascribed to the initial barrier of forming soluble polysulfides in the electrolyte, which in turn serve as an electron shuttle between the electronically conductive carbon matrix and the Li2S particles. Consistent with this hypothesis, Meini et al.36 found that the high
potential required in the first charging step of Li$_2$S cathodes can be eliminated in the presence of redox-active additives. Figure 3a shows the initial charging of a Li$_2$S cathode against a Li anode (Li/Li$_2$S half-cell) at rates of C/10 (blue line) and 1 C (red line), with the voltage initially increasing to potentials of ≈3.4 V$_{Li}$, and ≈3.9 V$_{Li}$, respectively, followed by a sharp decrease to a lower voltage plateau region. At the rate of C/10 (blue line), two charging plateaus at ≈3.2 and at ≈3.5 V$_{Li}$, are observed until the charging capacity approaches its theoretical value of 1165 mAh/g$_{Li_2S}$, at which point the voltage increases to ≈4.2 V$_{Li}$, where the current is sustained by the continuous oxidation of the DOL/DME electrolyte. On the other hand, at a rate of 1 C, the charging voltage strongly fluctuates and the charging process continues indefinitely between 2.5 and 3.5 V$_{Li}$, which we ascribe to the intermittent formation of lithium dendrites at this rather high current density of 2.3 mA/cm$^2$ (dendrite formation was shown to occur at >1 mA/cm$^2$). This is evidenced by SEM/EDS analysis of the middle separator removed from the Li/Li$_2$S cell after 1C charging (Fig. 4a). The separator was severely penetrated by lithium dendrites with a spot-size of 50 μm or more, and EDS mapping shows that these spots have a high oxygen content, indicating lithium oxides, hydroxides, or carbonates formed during air exposure of the separator (the separator was intentionally exposed to air to oxidize metallic lithium dendrites). These results confirm that the high current density during 1 C charging (2.3 mA/cm$^2$) leads to severe dendrite formation if metallic lithium used as anode.

As one would expect, lithium dendrite formation at high C-rate can be avoided during initial charging of a Li$_2$S cathode in Si/Li$_2$S full-cells, as evidenced by the smooth charging profile at 1 C in full-cells shown in Figure 3b (red line), where the potential is referenced against a metallic lithium reference electrode (using a three-electrode cell). Again, the capacity obtained as the potential reaches 4 V$_{Li}$ is close to the theoretical capacity of the Li$_2$S cathode. In order to confirm that Li$_2$S is oxidized completely during the first activation cycle and to determine whether the lower and upper plateaus at the C/10 charging profile in the Li/Li$_2$S half-cell (blue line in Fig. 3a) are indeed related to Li$_2$S charging, in-situ XRD analysis was carried out with a Li$_2$S cathode and a lithium metal counter electrode. Figure 5a shows the charging potential profile (vs. lithium) for a Li$_2$S cathode at C/10 in the in-situ XRD cell, which is in excellent agreement with the charging profile obtained with a standard Swagelok cell (see Fig. 3a, blue line). The labels placed along the charging curve (letters a - i in Fig. 5a) mark the collection of the XRD diffractograms shown in Fig. 5b (note that the diffractograms were acquired over a time of 9 minutes during cell charging). As expected, sharp peaks corresponding to the (111) and (200) diffractions of Li$_2$S are observed at the beginning of the charging process (a in Fig. 5b), then gradually decrease during the first charging plateau at ≈3.2 V$_{Li}$ (b – d in Fig. 5b), and remain visible throughout the second charging plateau of ≈3.5 V$_{Li}$ (e and f in Fig. 5b). The Li$_2$S diffraction peaks only disappear after the second charging plateau, i.e., after having reached 85–90% of the theoretical Li$_2$S charge capacity (g – i in Fig. 5b). This may be compared to the study by Cañas et al. who observed the disappearance of Li$_2$S diffractions during the charge of a discharged S cathode at already ≈50% of the charging capacity, which is most likely due to the much smaller Li$_2$S particles formed during S
Figure 4. [a] SEM image of the middle separator (out of three layers) of a Li/Li2S half-cell after initial charging at 1 C as shown by the red curve in Fig. 3a. [b] EDS mapping of carbon, oxygen, and sulfur of a lithium dendrite feature in the separator, whereby the high oxygen signal at the location of the dendrite originates from lithium which was deliberately exposed to air in order to oxidize it. The C-rates are calculated based on \( C_{\text{theoretical}} = 1165 \text{ mAh/gLi}_2\text{S} \) for the Li2S cathode.

The appearance and growth of new diffraction peaks (marked by * in Fig. 5b) can be observed at already \( \approx 60\% \) of charging (d in Fig. 5b), developing into sharp diffraction peaks after \( \approx 90\% \) of charging (g in Fig. 5b), which suggests the formation of large crystallites. These peaks must be related to the formation of crystalline sulfur, even though their positions do not exactly match the PDP database, indicating the formation of a new crystalline phase of sulfur. A similar observation was reported by Cañas et al., who reported sulfur reflections after \( \approx 80\% \) of charge of a previously discharged sulfur cathode, with diffraction patterns which were also different from the PDP database. Furthermore, Nelson et al. also observed the formation of crystalline sulfur after \( \approx 80\% \) charging of a discharged sulfur cathode. These findings, however, contradict the in-situ XRD study by Yang et al., where no crystalline sulfur is observed even after complete charging of their Li2S cathode; the origin of this discrepancy is unfortunately not clear.

In summary, the analysis of Figure 5 suggests that the charging process in the first plateau at \( \approx 3.2 \text{ V}_L \), which extends to \( \approx 60\% \) of the charging, can be assigned to the transformation of Li2S to lithium polysulfides and possibly small amounts of sulfur, as the potential is sufficiently high to oxidize polysulfides to sulfur. After the second charging plateau (g in Fig. 5), all Li2S diffraction peaks have vanished and sharp diffraction peaks related to crystalline sulfur appear (at around \( \theta = 12.8^\circ \)), indicating the formation of large sulfur crystallites in the charged Li2S cathode.

The formation of large crystalline sulfur domains after charge of the Li2S cathode was verified by ex-situ SEM/EDS analysis of the Li2S cathode after charging to a cutoff potential of 4V Li at C/10, i.e., after nearly 100\% of the theoretical charge was obtained. For this investigation, the cell was disassembled inside a glove box, washed with DME to remove any residual polysulfides from the cathode, and then the electrode transferred into ambient air in order to convert potentially remaining Li2S into Li2CO3, LiOH, and Li2O; subsequently, the sample was transferred into the SEM. Strikingly, as shown in Fig. 6a, the surface of the cathode was covered with large sheets of sulfur, as confirmed by the EDS elemental mapping: the sulfur map matches the SEM image (compare Figs. 6a and 6c), while no common patterns are observed between the oxygen map and the SEM image (compare Figs. 6a and 6d), which after air exposure could only be the case for elemental sulfur. The sulfur sheets extend over several hundreds of micrometers across the cathode surface, whereby imprints from the separator can be observed on the sulfur sheets. The cross-section of the cathode was examined after bending of the electrode, as shown in Fig. 6b. Empty pockets inside the cathode electrode can be clearly seen, the sizes of which are consistent with the initial size of
the Li$_2$S powder used to prepare the Li$_2$S cathode, which is consistent with the absence of Li$_2$S diffraction peaks after charging (Fig. 5).

Analogous to our study, the formation of large crystalline sulfur domains at the cathode/separator interface upon charging of a discharged sulfur electrode was also observed by Cañas et al., albeit with different shapes/morphology. We believe that the accumulation of sulfur at the cathode/separator interface during the last stages of the charging process is most likely due to the oxidation of dissolved polysulfides (solubilities of 0.1 to 1 mol/l in the electrolyte) contained inside the separator (rather than inside the cathode) during the final stages of charging: under this condition, the high cathode potential will cause the rapid and highly localized oxidation of polysulfides which are stored inside the separator region once they reach the cathode/separator interface, thereby forming a deposit at this very interface.

**Activation and cycling of Si/Li$_2$S full-cells.**—The activation and subsequent cycling of Si/Li$_2$S full-cells was investigated using Si/C anodes and Li$_2$S cathodes of theoretical capacities of $\approx$2.1 and $\approx$2.3 mAh/cm$^2$, respectively. In order to monitor the charge/discharge behavior of each electrode, the Si/Li$_2$S full-cells were assembled with a metallic lithium reference electrode in a three-electrode cell. The questions to be addressed were: i) whether the polysulfide shuffling currents would be low enough to allow for a complete charging of the Si/C anodes; ii) whether the high voltages at 1 C activation ($\approx$3.3/$\approx$3.5 V$_{Li}$ in the 1$^{st}$/2$^{nd}$ charging plateau; red line in Fig. 3b) compared to C/10 activation ($\approx$2.5/$\approx$3.1 V$_{Li}$ in the 1$^{st}$/2$^{nd}$ charging plateau; blue line in Fig. 3b) would affect the subsequent cycling stability, as activation at lower potentials was suggested to improve cycle-life, and iii) whether the long-term cycling stability of Si/Li$_2$S full-cells would be comparable with that of Li/Li$_2$S half-cells.

The Si/Li$_2$S full-cells were subjected to an initial activation from OCV ($\approx$0.3 V$_{cell}$) to a cell voltage of 3.8 V$_{cell}$ at two different rates, viz., C/10 (Fig. 7a) and 1 C (Fig. 7b), followed by continuous cycling between 1.3 and 2.8 V$_{cell}$ at C/5 rate. Figures 7a and 7b show the potential variation of the Li$_2$S cathodes vs. Li reference (curve 1, dashed blue line), the cell potential of the Si anodes vs. the Li$_2$S cathodes (curve 2, black line), and the potential of the Si anodes vs. Li reference (curve 3, dashed red line). Examining the first activation cycle at both C/10 and 1 C (initial charging panels in Figs. 7a and 7b, respectively), it is clear that the potential of the Si anodes is gradually lowered to $\approx$0.5 V$_{Li}$, where lithium ion intercalation will occur. The fact that the Si anode potentials decrease faster to below 0.5 V$_{Li}$ at 1 C (at $\approx$120 mAh/g$_{Li2S}$; dotted red line in Fig. 7b) compared to charging at C/10 (at $\approx$320 mAh/g$_{Li2S}$; dashed red line in Fig. 7a) is ascribed to the polysulfide shuttling current, which consumes a larger fraction of the charging current at the lower C-rate. At the end of the activation cycle, the Si anode potentials reach $\approx$0.1 V$_{Li}$, which according to Fig. 2b would correspond to a $\approx$50% charge of the Si anode ($\approx$1 mAh/cm$^2$). The missing charge compared to the expected $\approx$2.1 mAh/cm$^2$ (s. above) must be caused by the irreversible lithium loss for SEI formation. This is consistent with the only $\approx$50% theoretical cell capacity obtained in the second discharge/charge cycle at C/5 shown in Fig. 7: $\approx$550 mAh/g$_{Li2S}$ corresponding to $\approx$1.1 mAh/cm$^2$ at C/10 and $\approx$500 mAh/g$_{Li2S}$ corresponding to $\approx$1.0 mAh/cm$^2$. If compared with the Si anode half-cell data at the same current density (red lines in Fig. 2b), a charge/discharge capacity of $\approx$1.0–1.1 mAh/cm$^2$ is consistent with the observed Si anode potentials in the 2$^{nd}$ cycle, ranging between $\approx$0.12 and $\approx$0.5 V$_{Li}$ (s. C/5 segments in Fig. 7). These results clearly indicate that the capacity of the cell is limited by the Li$_2$S cathode due to a large irreversible lithium loss during the first charging cycle, while only about $\approx$50% of the anode’s capacity is used. Consequently, we expect that the Si/Li$_2$S full-cell performance will improve by applying an excess cathode capacity of Q$_{Li2S}$/Q$_{Si}$ between 1.5/1 and 2/1, which we will explore in future experiments.

The Li$_2$S cathode potential profiles during activation (blue dashed lines in Fig. 7) are essentially identical to those shown in Fig. 3b, except that potential oscillations are observed toward the end of the C/10 charging curve (dashed blue line in Fig. 7a). Indeed, we have
frequently observed these potential oscillations during charging at low C-rates, and Fig. 7a clearly shows that it is caused by the Li2S cathode and not the anode electrode. The fact that these oscillations appear in the second charging plateau, where we had observed the onset of the formation of crystalline sulfur phases (see Fig. 5) suggests that they are related to the formation of current-blocking sulfur domains at the separator/cathode interface (see Fig. 6). The absence of these oscillations at the higher rate of 1 C would then suggest that the formation of large sulfur sheets might be suppressed at higher rates, which could be explained by fact that the cathode potential in that case is far above the potential required for the complete reduction of polysulfides to sulfur, so that the polysulfide concentration in the electrolyte decomposition products at the initially high voltages that could compromise cycle-life. The higher coulombic efficiency of the cells cycled at C/5, independent of the activation procedure (red and black lines in Fig. 8a), is indicative of significant polysulfide-shuttle currents, which play a lesser role at the higher C-rate. After 70 cycles, the cells activated at C/10 and cycled at C/5 have a remaining capacity instead of at 1 C (see Fig. 7), which might prevent the formation of electrolyte decomposition products at the initially high voltages that could compromise cycle-life. The higher coulombic efficiency of the cells cycled at 1 C (gray lines in top panel of Fig. 8a) compared to the cells cycled at C/5, independent of the activation procedure (red and black lines in Fig. 8a), is indicative of significant polysulfide-shuttle currents, which play a lesser role at the higher C-rate. After 70 cycles, the cells activated at C/10 and cycled at C/5 have a remaining capacity
of 280 mAh/gLi2S, (≈400 mAh/gS). To our knowledge, our study is the first to examine the long-term stability of Si/Li2S full-cells based on Li2S powder based cathodes and Si based anodes. The only related study is the work by Yang et al.40 who cycled Si anodes with Li2S cathodes obtained by lithiation of a sulfur cathode with n-butyllithium, observing much higher capacity fading (to ≈250 mAh/gLi2S after only 20 cycles at a similar rate of C/3).

On the other hand, Si/S full-cell data have been obtained combining electrochemically pre-lithiated Si anodes with S cathodes. For the latter configuration, Elazari et al.29 demonstrated ≈380 mAh/gS after 60 cycles at C/5, and Brückner et al.1 showed ≈400 mAh/gS after 1400 cycles at C/2 (≈700 mAh/gS after 70 cycles at C/2). They also showed increased capacity fading with increasing C-rate for Li2S half-cells, while high C-rates of a large number of cycles could be maintained with Si/S full-cells based on S cathodes and pre-lithiated Si anodes, which they ascribed to both a larger irreversible electrolyte loss at the lithium anode and/or lithium dendrite formation. Without providing any proof, their hypothesis would suggest that the rate capability of Si/S or Si/Li2S full-cells would be higher than that of Li/S or Li/Li2S half-cell. That is indeed the case is shown by our Si/Li2S full-cell tests, which demonstrate the same capacity retention of 350 mAh/g (≈250 mAh/gLi2S) after 70 cycles, independent of whether were cycled at 1 C or C/5 (gray and black lines in Fig. 8a, respectively). Thus, we can provide for the first time an unambiguous proof that the poor rate capability in Li/S or Li/Li2S half-cells is caused by the lithium anode and that the kinetics of the sulfur cathode is much faster than previously assumed based on half-cell data.

Furthermore, the fact that the capacity retention of Si/Li2S full-cells is the same at C/5 and 1 C demonstrates that capacity fading is not related to total time, but to the number of cycles, which points toward irreversible lithium loss, originating from SEI expansion/contraction during each cycle. This is indeed supported by a comparison of the capacity retention between Si/Li2S full-cells and Li/Li2S half-cells at C/5 (s. Fig. 8b): while the initial capacities are quite similar for half-cells, the capacity retention of half-cells is superior (≈550 vs. ≈400 mAh/gS after 70 cycles), which supports the above hypothesis. Active lithium loss into the SEI. Here it may be noted that the capacity retention of our Li/Li2S half-cells compares reasonably well with that shown previously by Yang et al.29 (≈650 mAh/gS after 50 cycles at C/10) and Cai et al.41 (≈550 mAh/gS after 45 cycles at C/5).

Conclusions

Li2S cathodes were prepared from as-received Li2S powder (∼20 μm particle size) and in-situ XRD half-cell measurements clearly showed that Li2S could be completely decomposed during the first charge and that crystalline sulfur was being formed. This was confirmed by ex-situ SEM/EDX, revealing the presence of very large sulfur sheet (>100 μm) located at the separator/cathode interface, which we believe is caused by the oxidation of dissolved polysulfides present in the separator.

Li2S cathodes were also tested in full-cells using Si/C composite electrodes without any pre-treatment. While Li/S and Li/Li2S half-cells have been shown in the literature to have a poor capacity retention at high C-rates, we could demonstrate for the first time that the capacity and the capacity fading of Si/Li2S full-cells is identical for C/5 and 1 C. This suggests that the apparently poor rate capability of sulfur cathodes tested in half-cells is caused by the lithium electrode and that the intrinsic charge/discharge kinetics of sulfur cathodes are much larger than previously thought.

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References

1. P. G. Bruce, S. A. Freunberger, L. J. Hardwick, and J. M. Tarascon, Nat. Mater., 11, 881 (2012).
2. F. T. Wagner, B. Laksmanan, and M. F. Mathias, J. Phys. Chem. Lett., 1, 2204 (2010).
3. K. M. Abraham and Z. Jiang, J. Electrochem. Soc., 143, 1 (1996).
4. M. B. R. Rao, U. S. Pat, 341354 (1968).
5. R. D. Rauh, K. M. Abraham, G. F. Peterson, J. K. Surprent, and S. B. Brunner, J. Electrochem. Soc., 126, 523 (1979).
6. K. G. Gallagher, S. Goebel, T. Greszler, M. Mathias, W. Oelerich, D. Erogluab, and V. Sinivasan, Energy Environ. Sci., 7, 1555 (2014).
7. R. D. McCloskey, A. Valery, A. C. Luntz, S. R. Gowda, G. M. Wallraff, J. M. Garcia, G. V. Chase, and D. Addison, J. Phys. Chem. C, 117, 11977 (2013).
8. S. M. Obrovac, L. Christensen, J. Power Source, 191, 5223 (2009).
9. S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Bard, and P. G. Bruce, Angew. Chem. Int. Ed., 50, 1 (2011).
10. M. M. O. Thotiyl, S. A. Freunberger, Z. Peng, and P. G. Bruce, J. Am. Chem. Soc., 135, 494 (2013).
11. Y. Mikhaylik, I. Kovaliev, R. Schock, K. Kumaresan, J. X. and J. Affinito, ECS Transactions, 25, 335 (2010).
12. J. M. Tarascon and M. Armand, Nature, 413, 359 (2001).
13. W-J. Zhang, J. Power Sources, 196, 13 (2011).
14. C. T. Wang, J. Z. Gong, J. Power Sources, 195, 2617 (2012).
15. H. Althues, K. U. Schwenke, M. Piana, H. Beyer, L. Lange, and J. Joumakis, J. Electrochem. Soc., 156, A694 (2009).
16. X. Liang, D. Bartoli, J. F. Nazar, Nat. Mater., 8, 500 (2009).
17. R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, and D. Aurbach, Adv. Mater., 23, 5641 (2011).
18. X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, and L. F. Nazar, Nat. Comp., article number 5082 (2015).
19. D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. S. Kelley, and J. Affinito, J. Electrochem. Soc., 156, A694 (2009).
20. K. Dokko, N. Tsiouvaras, K. Yamauchi, M. Tsuchiya, A. Yamazaki, E. Takashima, J. Wurck, K. Ueno, S. Seki, N. Serizawa, and M. Watanabe, J. Electrochem. Soc., 160, A1304 (2013).
21. J. Schuster, G. He, B. Mandleimier, Y. Kim, K. T. Lee, T. Bein, and L. F. Nazar, Angew. Chem. Int. Ed., 51, 3591 (2012).
22. J. M. Tarascon and M. Armand, Nature, 413, 359 (2001).
23. N. Liu, L. Hu, M. T. McDowell, A. Jackson, and Y. Cui, ACS Nano, 5, 6487 (2011).
24. J. Brückner, S. Thiene, F. Böttger-Hiller, I. Bauer, H. T. Grossmann, P. Strubel, H. Althues, S. Spange, and S. Kaskel, J. Electrochem. Soc., 159, 11478 (2013).
25. S. Meini, N. Tsiouvaras, K. U. Schwenke, M. Piana, H. Beyer, L. Lange, and H. A. Gusteiger, Phys. Chem. Chem. Phys., 15, 11478 (2013).
26. S. Meini, R. Elazari, A. Rosenman, A. Garsuch, and D. Aurbach, J. Phys. Chem. Lett., 5, 915 (2014).
27. D. Aurbach, E. Zingrad, Y. Cohen, and H.eller, Solid State Ionics, 140, 405 (2002).
28. N. A. Canas, S. Wolf, N. Wagner, and K. A. Friedrich, J. Power Source, 226, 313 (2013).
29. J. Nelson, S. Misra, Y. Yang, A. Jackson, Y. Liu, Haifang Wang, H. Dai, J. M. Adams, Y. Cui, J. Am. Chem. Soc., 134, 6337 (2012).
30. J. Nelson, M. T. McDowell, A. Jackson, J. J. Cha, S. S. Hong, and Y. Cui, Nano Lett., 10, 1486 (2010).
31. K. Cai, M-K. Song, E. J. Cairns, and Y. Zhang, Nano Lett., 12, 6474 (2012).