Thermal batteries are an established primary battery technology, which finds use in applications such as emergency power supplies in aircraft. Such applications require a constant power to be drawn over a length of time.

Typically, thermal batteries consist of a cathode, a molten salt electrolyte, separator and anode. A pyrotechnic source is used to heat the battery above the melting point of the electrolyte, which brings about a high ionic conductivity in the electrolyte. The KCl-LiCl eutectic is a battery above the melting point of the electrolyte, which brings about thermal stability of the other battery components and the high ionic conductivity in the electrolyte. The KCl-LiCl eutectic is a common choice of electrolyte, due to its melting point being compatible with the thermal stability of the other battery components and the low solubility of other battery components in the electrolyte. The anode is usually a lithium alloy, such as Li13Si4, which has a high melting point, enabling operation in high temperature batteries. Li13Si4 also possesses a high lithium ion conductivity. MgO is a typical separator and transition metal sulfides are usually used as the cathode.

The most commonly used cathode materials are transition metal disulfides MS2 (where M = Co, Ni and Fe). However, understanding the evolution of crystalline phases upon battery discharge has been hindered due to the high temperature operation of these batteries. Here we report an experiment that simultaneously collects powder neutron diffraction and electrochemical data as the battery is discharged. Four regions are observed in the diffraction data and four different cobalt containing phases are observed. Multi-phase Rietveld refinement has been used to monitor the evolution of phases during discharge and this is linked to the battery discharge profile. A new discharge mechanism has been proposed which involves hexagonal CoS instead of Co3S4, and the increase in unit cell parameters on discharge suggests the formation of a sulfur deficient solid solution before transformation to Co9S8. This behavior seems reminiscent of that of NiS2 suggesting that the discharge mechanisms of transition metal disulfides may have more similarities than originally thought.

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Experimental

Prior to the in situ neutron diffraction experiment, a smaller cell was assembled using CoS₂ (cathode, 0.17 g, 14.0 mmol) as the cathode, Li₁₃Si₄ (0.29 g, 14.3 mmol) as the anode, MgO as the separator and the LiCl-KCl eutectic as the electrolyte. The anode, cathode and electrolyte/separator were pressed into pellets separately and then loaded into a Swagelok type assembly in an argon-filled glove box. This enabled electrochemical testing to be carried out ex situ at 520°C in a muffle furnace, using a Maccor battery tester (model 5300). The battery was tested galvanostatically, applying a current density of 127.3 mA cm⁻².

Time of flight neutron diffraction data were collected on the Polaris diffractometer at the ISIS neutron source, Rutherford Appleton Laboratory, UK. Polaris is a high intensity medium resolution diffractometer with a large area of detector coverage. Combined, these lead to a very high count rate which lends itself well to the fast data collection required to study battery discharge. The St Andrews Conductivity Rig, which has been specially developed for the simultaneous collection of neutron diffraction and electrochemical data in a controlled atmosphere, which has been described elsewhere, was used for this experiment.¹⁴ The sample holder of the St Andrews Conductivity Rig was adapted for this experiment to use thin vanadium plate as both current collectors for the electrochemical measurements and for holding the sample in place. Vanadium is an excellent choice in this respect, due to its neutron scattering length of −0.38 fm, meaning that the intensities of the Bragg reflections from the sample holder/current collector are very weak, and make negligible contribution to the diffraction pattern compared to the rest of the battery components.

For the neutron diffraction experiment, Li₁₃Si₄ (anode, 0.22 g, 1.1 mmol), a mixture of LiCl-KCl eutectic (electrolyte), LiBr (separator) and CoS₂ (cathode, 0.64 g, 3.6 mmol) were pressed sequentially into pellets of diameter 23.6 mm and an approximate thickness of 1–2 mm, which were kept under argon until required due to their air and moisture sensitivity. For each neutron diffusion experiment one single cell battery was loaded into the St Andrews Conductivity Rig in an Argon-filled glove box, then the rig was placed in a Rutherford Appleton Laboratory designed furnace which was mounted on the Polaris diffractometer. A Type-K thermocouple was placed inside the rig, approximately 2 cm above the sample holder and was used to control the temperature of the battery during the experiment. All diffraction measurements were carried out under flowing argon due to the air and moisture sensitivity of these samples.

A powder neutron diffraction pattern was collected initially for ~1 hour at room temperature from the undischarged battery (where the molten salt electrolyte would be solid). Following this, a series of diffraction patterns of 5 minutes duration were collected while the CoS₂ cell was then heated up to 520°C at 10°C/minute in order to monitor any phase changes and confirm melting of the LiCl-KCl eutectic. Following this, the potentiostatic cell discharge was started and over the next ~18 hours a large number of diffraction patterns of 5 minutes duration were collected as the cell discharged. During the discharge, electrochemical data were collected potentiostatically using a Kikusui electrochemical interface.

During the subsequent data reduction, diffraction patterns corresponding to iso-potentials in the discharge profile were summed together into single datasets to improve counting statistics and thus allow quantitative phase analysis to be carried out in the Rietveld refinement. Rietveld refinement was carried out using GSAS.¹⁵,¹⁶ Film plots of diffraction data were created using the WinPlotr function in Fullprof.¹⁷,¹⁸

Results and Discussion

In order to determine the potentials of interest before the combined in situ neutron diffraction and battery discharge experiment, an ex situ battery discharge experiment was carried out on a CoS₂ cell (with a Li₁₃Si₄ anode and a LiCl-KCl eutectic electrolyte). This test was carried out at 520°C, which is sufficiently above the melting point of the KCl-LiCl eutectic for the electrolyte to achieve a high ionic conductivity. The cell was discharged galvanostatically and the resulting battery discharge profile is shown in Figure 2. Figure 2 clearly shows the presence of two regions, one at 1.45 V and one at 1.05 V. This is in agreement with the two plateaux observed at around 1.75-1.6 V and ~1.13 V when tested with a Li-Si anode and a LiBr-KBr-LiCl eutectic electrolyte at 500°C.⁴

Figure 3 shows the room temperature powder neutron diffraction pattern obtained from the battery before discharge. The broad features in the background are due to the amorphous quartz sample holder. Several phases were identified in the diffraction pattern

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**Figure 1.** Crystal structures for different cobalt sulfides. (a) CoS₂ with the pyrite structure, (b) Co₃S₄ with the spinel structure, (c) CoS with the NiAs structure and (d) Co₉S₈. Yellow atoms are sulfur, dark blue atoms are cobalt in octahedral sites and light blue is cobalt in tetrahedral sites.

**Figure 2.** Ex situ battery discharge profile using CoS₂ as a cathode at 520°C and a current density of 127.3 mA cm⁻².
and these include CoS₂, MgO, KCl, LiCl and LiF. CoS₂ has the pyrite structure, whilst all other phases adopt the rock-salt structure. Several unindexed peaks could be observed in the diffraction pattern, the most prominent at 1.67 Å which could be indexed to a 5.377(4) Å cubic unit cell, indicating a LiBr₁₋ₓClₓ solid solution and this suggests that halide exchange occurs in the eutectic salt. The unit cell parameters of the phases present at room temperature are given in Table I. No peaks were observed from the Li₁₃Si₄ anode, presumably due to the loss in crystallinity during processing and the fact that it adopts a low symmetry structure with a large unit cell.

After room temperature data collection, the cell was heated to a temperature above the melting point of the LiCl-KCl molten salt electrolyte. Once the cell had reached 520°C, the battery was discharged potentiostatically. The resulting powder diffraction data collected during discharge are shown in Figure 4 as a film plot. This indicates four different regions, one region between 1.8 and 1.7 V, a second region between 1.7 and 1.5 V, the third region between 1.5 and 1.25 V and the final region between 1.25 and 1 V.

In order to both identify and quantify the phases present upon discharge, Rietveld refinement was carried out. The structured background in the diffraction patterns arising from the amorphous quartz vessel of the Conductivity Rig was modelled using seven diffuse scattering parameters based on the Si-O, Si-Si and O-O interatomic distances in quartz. In addition a further four parameters using a reciprocal linear interpolation function were added to account for the overall decrease in background intensity over the d-spacing range used. In the latter stages of the refinements all background parameters were fixed during the structure refinement. The low signal to noise ratio in the powder diffraction patterns is due to the relatively thin battery used during the experiment in order to obtain a more realistic electrochemical performance. The separator, MgO, was present in all diffraction patterns. Figures 5a–5d show multiphase Rietveld fits for data collected during the CoS₂ cell discharge, at potentials of 1.6 V, 1.4 V, 1.2 V and 1.1 V. At 1.6 V (Figure 5a), no CoS₂ is present in the diffraction pattern, and only CoS and Li₂S are observed. From Figure 4a clear expansion in the “CoS” unit cell is observed as evidenced by the movement of peaks at d-spacings of ∼1.7, ∼2.0 and ∼2.6 Å which could indicate lithium incorporation into this phase or sulfur loss. Due to the relatively fast data collections, the cell parameter evolution in this region cannot be accurately determined; however, the expansion is significant approaching 1% for both a and c based upon the observed peak shifts. Comparing the unit cell volume per Co atom, CoS₀S₈ is about 3.5% larger than CoS, suggesting that CoS loses S to form CoS₁₋ₓ, as its composition moves toward CoS₀S₈. Figure 5b shows the diffraction data collected at 1.4 V. The CoS₁₋ₓ phase is no longer present in the diffraction pattern, indicating that the “CoS₁₋ₓ” phase has converted to CoS₀S₈. At 1.2 V (Figure 5c) CoS₀S₈ is still present in the diffraction pattern, but by 1.1 V (Figure 5d), Co is now present in the diffraction pattern. However, at this voltage, the battery discharge is not complete as some CoS₀S₈ remains in the diffraction pattern. At this stage the voltage is below the cutoff point for practical applications, so the experiment was stopped. The resulting unit cell parameters for the different crystalline phases present during battery discharge at 520°C are given in Table II.

The phase fractions extracted from the multiple phase Rietveld refinements are plotted in Figures 6a and 6b. Figure 6a shows the phase fraction obtained from Rietveld refinement plotted with the battery discharge profile obtained during the in situ experiment, whilst Figure 6b shows the phase fraction as a function of voltage. Between 1.8 and 1.6 V, the plateau observed in the electrochemical data corresponds to the CoS₂ to CoS + Li₂S transition. A slope then occurs in the battery discharge profile between 1.6 V and 1.4 V and the CoS (via CoS₁₋ₓ) to CoS₀S₈ transformation is responsible for this transition.

| Phase | Unit Cell Parameters at room temperature(Å) |
|-------|---------------------------------------------|
| MgO   | 4.20843(9)                                  |
| CoS₂  | 5.5332(3)                                   |
| KCl   | 6.2962(4)                                   |
| LiCl  | 5.14194(14)                                 |
| LiF   | 4.0287(3)                                   |
| LiBr₁₋ₓClₓ | 5.3777(4)                               |

| Phase | Unit Cell Parameters at 520°C (Å) |
|-------|-----------------------------------|
| MgO   | a = 4.23580(10)                  |
| Li₂S  | a = 5.7949(7)                   |
| CoS₂  | a = 5.5713(7)                   |
| CoS   | a = 3.4162(5)                   |
| CoS₀S₈| a = 10.0092(9)                  |
| Co    | a = 3.5669(15)                  |

Figure 3. Multiphase Rietveld fit for data collected at room temperature on the CoS₂ cell.

Figure 4. Film plot of powder neutron diffraction data collected upon discharge of a thermal battery using CoS₂ as the cathode. The y-axis is not a linear function of voltage, but data-set number.
Finally, the transformation of Co₉S₈ to Co accounts for the final plateau, from 1.2 V to 1.1 V.

The discharge mechanism previously outlined by Preto et al. is given in Equation 1:

\[
\text{CoS}_2 \rightarrow \text{Co}_3\text{S}_4 + \text{Li}_2\text{S} \\
\text{Co}_3\text{S}_4 + \text{Li}_2\text{S} \rightarrow \text{Co}_9\text{S}_8 + \text{Li}_2\text{S} \\
\text{Co}_9\text{S}_8 + \text{Li}_2\text{S} \rightarrow \text{Co} + 8/9\text{Li}_2\text{S}
\]  [1]

However, during our experiment we see no evidence for the formation of Co₃S₄. Instead, we see the presence of the hexagonal CoS related phase. As can be seen in Figure 4, the cell parameters of the hexagonal CoS phase increase during discharge. The most likely cause for this increase in cell parameter is sulfur loss, as further discharge leads to a cobalt sulfide with lower S content, Co₉S₈. This leads us to propose a new discharge mechanism:

\[
\text{CoS}_2 + 2\text{Li} \rightarrow \text{CoS} + \text{Li}_2\text{S} \\
\text{CoS} + 2/9\text{Li} \rightarrow 1/9\text{Co}_9\text{S}_8 + 1/9\text{Li}_2\text{S} \\
1/9\text{Co}_9\text{S}_8 + 16/9\text{Li} \rightarrow \text{Co} + 8/9\text{Li}_2\text{S}
\]  [2-4]

Interestingly, this proposed discharge mechanism also has similarities to the mechanism recently determined during the in situ discharge of a thermal battery using a NiS₂ cathode. In both instances, the first discharge step involves MS₂ → MS (M = Co, Ni), which is accompanied by an increase in cell parameter in the MS phase associated with sulfur deficiency. Therefore, our in situ battery discharge experiments carried out at high temperature suggest that there are more similarities in the discharge mechanism for MS₂ (M = Co, Ni) than originally thought, as based on the work of Preto et al. The discharge mechanisms previously proposed by Preto et al. were different, depending on the transition metal present in the cathode.
Conclusions

In this experiment, we have probed the evolution of the crystalline phases upon discharge of a thermal battery employing CoS₂ as a cathode, by collecting neutron powder diffraction data and electrochemical data simultaneously. We have proposed a new discharge mechanism which includes CoS and does not involve the Co₃S₄ spinel phase. There is an increase in cell parameter of the CoS phase during discharge and this warrants more detailed investigation. The most likely reason for this increase in cell parameter is sulfur loss to form lithium sulfide on discharge. The identification of CoS in the discharge mechanism of CoS₂ cathodes is significant as it suggests that the CoS₂ and NiS₂ discharge mechanisms are more similar than originally thought, as both mechanisms have now been shown to include a MS phase (where M = Co or Ni) with the NiAs structure, and in both cases there is an increase in cell parameter.

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