Derivation of an Iron Pyrite All-Solid-State Composite Electrode with Ferrophosphorus, Sulfur, and Lithium Sulfide as Precursors

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In order to address the poor energy density of bulk all-solid-state lithium-ion batteries a new composite electrode preparation method is proposed. This study demonstrates the concurrent synthesis of the FeS2 active material and a glass electrolyte which is similar to the (100-x)P2S5:xLi2S system of glass electrolytes. This is accomplished through the successive mechanochemical and thermal treatments of Fe2P, S, and Li2S. The composite electrode’s ionic conductivity of 5.46 × 10−5 S cm−1 at 60°C and specific energy of 1.2 Wh g−1 versus a lithium metal anode suggest that this method may provide a more intimate solid-solid interfacial contact between active material and glass electrolyte. The results of this study provide a completely new perspective on the preparation of all-solid-state composite electrodes.

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Bulk all-solid-state composite electrode engineering conventionally approaches the problem of interfacial structuring from the perspective that the active material and the solid-state electrolyte must each be prepared separately and then combined via mechanical mixing. Wetting the porous electrode with a liquid electrolyte creates intimate interfacial contact. However, the power and energy density of bulk all-solid-state batteries suffer because a solid-state electrolyte cannot interface as intimately with the active material as a liquid electrolyte. For example, an all-solid-state electrode utilizing FeS2 and the P2S5-Li2S glass electrolyte had an active mass loading of only 32% in order to achieve FeS2’s theoretical capacity of 894 mA g−1. Similarly structured cells utilizing S or Li2S as the active material suffer from the same limitations. While the bulk all-solid-state battery architecture has demonstrated its value by enabling the reversible cycling of high capacity conversion active materials, further interfacial engineering should address how to achieve practical electrode level energy density.

Along these lines, isostatic pressing (HIP) was proposed as a method to densify composite electrodes with the P2S5-Li2S glass-ceramic for improved interfacial contact. HIP’ing is not appropriate for active materials which may be reactive or decompose at high temperatures. Pulsed laser deposition of P2S5-Li2S glass electrolyte coatings onto active material particles has also been suggested as a way to improve interfacial contact and increase active material mass loading. Another method involves mechanically preparing sulfur composite electrodes at a temperature above sulfur’s melting point so that sulfur can flow about P2S5-Li2S glass-ceramic electrolyte particles. An electrode prepared in such a manner was reported to deliver a specific energy in excess of 1000 Wh kg−1. Spark plasma sintering9 and impregnation of active material sols into macroporous 3D electrolyte membranes10–14 have also been suggested for all-solid-state batteries utilizing ceramic electrolytes other than the P2S5-Li2S system of glass-ceramics. Further, the development of polysulfophosphates has blurred the distinction between active material and solid-state electrolyte.15

In order to structure an intimate solid-solid interface this study proposes that the active material and glass electrolyte former can be synthesized concurrently as products of a single solid-state chemical reaction. Interfacial contact may then be dictated not only by the mechanical properties of the composite electrode components, but also by the process of phase nucleation and growth. In the study outlined here the concurrently synthesized active material and electrolyte former are suggested to be FeS2 and P2S5, respectively.

Historically, the reaction of iron pyrite (FeS2) with ferrophosphorus (Fe2P) at temperatures between 700 – 800°C was thought to produce P2S5 and FeS.16 In this two step process, Fe2S first thermally decomposes into FeS and S.17 Sulfur then reacts with FeP to form P2S5 and more FeS. P2S5 can also be synthesized by the direct reaction of S with Fe2P.18 Equation 1 proposes FeS2 and P2S5 as the byproducts for the reaction of S and Fe2P at a temperature of 350°C. The enthalpy of this reaction at standard state is −762.6 kJ mol−1 or −674 kJ mol−1 depending upon the source of the P2S5 data so it is expected that this reaction is thermodynamically favorable. The P2S5 component of this proposed composite can then be mechanochemically modified with Li2S to synthesize the 22.5P2S5:77.5Li2S glass electrolyte which will be intimately in contact with the FeS2 phase. Equation 2 outlines this reaction assuming that Equation 1’s reaction is complete with no other byproducts. This method should be contrasted with our previous FeS2 composite electrode preparation technique where FeS2 and carbon black are mixed with a pre-prepared 22.5P2S5:77.5Li2S glass electrolyte.1

2Fe2P + 13S → 4FeS2 + P2S5(350°C)  
2.5(4Fe2P + P2S5) + 77.5Li2S → 90FeS2 + 22.5P2S5 + 77.5Li2S 

Methods

All procedures to be outlined were conducted in a dry argon environment. The electrode composite was prepared via a three step process. First, 2 g total (2:13 molar ratio) of Fe2P (Aldrich, 99.5%) and Sulfur (Aldrich, 99.98%) were combined by planetary ball milling. Material was milled in an airtight 500 mL stainless steel jar (Across International) with two 16 mm diameter and twenty 10 mm diameter stainless steel balls (Across International) for 20 hours at 500 rpm. Second, the composite was heat treated in an evacuated flame sealed borosilicate glass ampoule at 350°C for 3 hours with controlled temperature ramping and cooling both taking 1 hour. Third, planetary ball milling was used to combine 0.5 g total (22.5:77.5 molar ratio) of the heat treated composite and Li2S (Aldrich, 99.999%, reagent grade). Material was milled in an airtight 100 mL agate jar (Across International) with fifty 6 mm diameter and twenty 10 mm diameter agate balls for 20 hours at 500 rpm. The materials resulting from the completion of the first, second, and third step are referred to as (BM), (BM + HT), and (BM + HT + BM) in the text and figures. BM is shorthand for ball mill while HT is shorthand for heat-treatment.

To assemble test cells, a 200 mg glass electrolyte pellet separator (ψ = 13 mm) was first pressed at 1 metric ton inside a polyethyleneketone (PEEK) lined Ti test cell die.21 The electrolyte used for the separator was the previously described mechanochemically prepared

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22.5P$_2$S$_5$:77.5Li$_2$S glass. For increased electronic conductivity, 10 wt% of carbon black (TimCal, C65) was added to the composite electrode using an agate mortar and pestle. 5 mg of the composite electrode was then pressed to one side of the glass electrolyte pellet at 5 metric tons and an LiIn alloy (FMC Lithium Corp., Lectro Max Powder 100 and Indium powder, Alfa Aesar, Puratronic 99.999%) was attached to the opposite side of the pellet at 1 metric ton. The LiIn alloy has a potential of 0.62 V vs. Li$^+$/Li for a limited compositional range so voltage profile figures are given with respect to both LiIn and Li metal. Calculations of specific energy assume Li metal as the anode and all specific capacities and current densities are given with respect to the total composite electrode mass including carbon black. The test cells were cycled at 60 °C under constant current constant voltage (CCCV) cycling parameters.

The composite electrode was characterized by Cu-Kα powder X-ray diffraction, FIB-SEM EDS analysis, cyclic voltammetry, and Raman spectroscopy. The FIB sample was prepared as previously described. Cyclic voltammetry was used to measure the electronic conductivity of the composite electrode by sweeping symmetric cells as presented in Figure 4a. To measure ionic conductivity, a composite electrode pellet without a carbon black additive (150 mg) was sandwiched between two layers of the 22.5P$_2$S$_5$:77.5Li$_2$S glass electrolyte (150 mg each) in order to block electron flow as presented in Figure 4b. A similar cell configuration was used previously, but here junction potentials and resistance to charge transfer are considered negligible at layer interfaces. The contributions from the electron-blocking glass electrolyte layers can be subtracted out by considering that 1/σelectron = R$_{cell} + 2/σ_{electrolyte}$. The ionic conductivity of the 22.5P$_2$S$_5$:77.5Li$_2$S glass electrolyte used in the experiment was measured to have an ionic conductivity of 2.91 × 10$^{-4}$ S cm$^{-1}$ at 25 °C and 1.297 × 10$^{-3}$ S cm$^{-1}$ at 60 °C. DC polarization measurements at 10 mV were used to calculate the ionic conductivity of the electrodes. The calculations use the stabilized current values because, after a period of transient decay, the stabilized current is thought to be totally ionic. Raman spectra were recorded using a JASCO NRS-3100 system equipped with a 532 nm laser at a power level of 0.1 mW focused through a 20× objective lens. Power levels higher than this were observed to cause sample degradation. Raman shift was calibrated using a silicon standard and accuracy was estimated to be ±7 cm$^{-1}$. As the dark color of the material led to weak Raman scattering, 15 accumulations of 45 seconds each were typically averaged to increase the signal-to-noise ratio.

**Results**

Powder XRD was used to identify the phases present over the course of the FeS$_2$ composite-electrode preparation. Figure 1 provides the XRD patterns for samples (BM), (BM + HT), and (BM + HT + BM). From the pattern for sample (BM), it was determined that FeP does not react with S during mechanical milling. After heat treating sample (BM) at 350 °C a solid-state reaction was observed to occur. The pattern for sample (BM + HT) has new peaks which can be assigned to iron pyrite (FeS$_2$) and orthorhombic FeP while peaks for FeP disappear. Three weak peaks corresponding to sulfur’s three strongest diffractions are also observed. Residual sulfur is consistent with the observation of sulfur crystallization on the inside surface of the evacuated glass ampoules after heat-treatment (Supporting Figure 1). After the addition of Li$_2$S, no new phases are observed in the pattern for sample (BM + HT + BM). Depending on the composition residual crystalline Li$_2$S is frequently observed when the (100-x)P$_2$S$_5$:xLi$_2$S glass is mechanochemically prepared, but no crystalline Li$_2$S peaks are observed here. This may be due to the amorphization of Li$_2$S or a reaction between Li$_2$S and a glass former. Diffraction peaks for FeS$_2$ and FeP are found to broaden and reduce in intensity after the second ball milling step which is consistent with the reduction of average crystallite size by mechanical grinding. Diffraction peaks for crystalline P$_2$S$_5$ are not observed in any of the samples.

**Figure 1.** Powder XRD patterns for the (BM), (BM + HT) and (BM + HT + BM) samples. Peaks are indexed to Fe$_2$P (open square), S (triangle), FeP (diamond), and cubic-FeS$_2$ (star).
Four main peaks are observed at 480 cm\(^{-1}\), Li\(_2\)S, and the 22.5P\(_2\)S\(_5\):77.5Li\(_2\)S glass electrolyte. Peaks at 422 cm\(^{-1}\) acted S in the composite\(^{28,29}\) while the peaks at 422 cm\(^{-1}\) and 340 cm\(^{-1}\) is compared to that for FeS\(_2\), Li\(_2\)S, and the 22.5P\(_2\)S\(_5\):77.5Li\(_2\)S glass electrolyte. The 422 cm\(^{-1}\) peak is attributed to residual S. The PS\(_4^{3−}\) ion, indicative of a glassy ionic conductor, has been reported at 420 cm\(^{-1}\). The 422 cm\(^{-1}\) peak attributed to FeS\(_2\) overlaps is superimposed with the PS\(_4^{3−}\) peak.

Raman spectroscopy provided in Figure 3 was used to characterize the ionic conductive component of the (BM + HT + BM) electrode. The Raman spectrum for the (BM + HT + BM) electrode is compared to that for FeS\(_2\), Li\(_2\)S, and the 22.5P\(_2\)S\(_5\):77.5Li\(_2\)S glass electrolyte. Four main peaks are observed at 480 cm\(^{-1}\), 422 cm\(^{-1}\), 378 cm\(^{-1}\), and 340 cm\(^{-1}\). The peak at 480 cm\(^{-1}\) is attributed to unreacted S in the composite\(^{28,29}\) while the peaks at 422 cm\(^{-1}\), 378 cm\(^{-1}\), and 340 cm\(^{-1}\) coincide with the peaks for FeS\(_2\). A peak at 420 cm\(^{-1}\) is typically assigned to the thiophosphate ion, PS\(_4^{3−}\), of the (100-x)P\(_2\)S\(_5\):xLi\(_2\)S system of glass-ceramic electrolytes.\(^{30}\) Observation of the PS\(_4^{3−}\) ion would confirm that the composite electrode contains the local structure of the glass electrolyte and indirectly suggests the formation of P\(_2\)S\(_5\) or another glass former. Qualitatively, the ratio of the 422 cm\(^{-1}\) to 378 cm\(^{-1}\) peak intensities is much smaller for FeS\(_2\) than it is for the electrode. The increase in the ratio of these peaks is attributed to the presence of PS\(_4^{3−}\). Unfortunately, the (BM + HT + BM) electrode powder exhibited poor Raman scattering so a meaningful peak deconvolution could not be performed. To substantiate our claim for the formation of a glassy electrolyte, the ionic transport of the mixed conductors using the same symmetric cell configuration presented in Figure 4b.\(^{31}\) However, for the (BM + HT + BM) sample we observed a significant amount of non-Ohmic current using the cyclic voltammetry method. For this reason, the ionic conductivity was measured by performing 10 mV DC polarization measurements on symmetric multi-layer test cells (Figure 4d). In the DC polarization method, the ionic conductivity is calculated by measuring the stabilized current after transient decay. It is noted that the transient current of the (BM + HT + BM) sample tested at 60 °C took far longer to decay than it did in other tests. The electronic conductivity was measured by the cyclic voltammetry method. As a control, a conventional composite electrode was prepared by mixing nano-sized natural pyrite and 22.5P\(_2\)S\(_5\):77.5Li\(_2\)S in a weight ratio of 56:44. This weight ratio corresponds to the theoretical weight ratio of the products in Equation 2. The natural FeS\(_2\) is the same as that used in a recent study by Son et al.\(^{32}\)

The electronic conductivity of a conventional composite electrode without carbon black additive is only 1.81 \times 10^{-5} S \text{ cm}^{-1} while the electronic conductivity of the (BM + HT + BM) composite electrode without carbon black is 4.94 \times 10^{-5} S \text{ cm}^{-1} (Figure 4e). The good electronic conductivity of the (BM + HT + BM) electrode is attributed to the presence of the unexpected FeP phase.\(^{33}\) On the other hand, the ionic conductivity of the conventional electrode is superior to that of the (BM + HT + BM) electrode. At 60 °C, the conventional electrode has an ionic conductivity of 2.82 \times 10^{-4} S \text{ cm}^{-1} while the (BM + HT + BM) electrode has an ionic conductivity of approximately 5.46 \times 10^{-4} S \text{ cm}^{-1} (Figure 4d) at 60 °C.

The results of constant current constant voltage (CCCV) cycling at 60 °C are provided in Figure 5. All specific capacities are normalized to the total mass of the composite electrode including carbon black. In anticipation of excess Li\(_2\)S utilization, the (BM + HT + BM) electrode was initially overcharged to provide an extra 114 mAh g\(^{-1}\)

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**Figure 3.** Raman spectroscopy of the (BM + HT + BM) sample compared to cubic-FeS\(_2\), Li\(_2\)S, and the 22.5P\(_2\)S\(_5\):77.5Li\(_2\)S glass electrolyte. Peaks at 422 cm\(^{-1}\), 378 cm\(^{-1}\), and 340 cm\(^{-1}\) are attributed to cubic-FeS\(_2\) while the peak at 480 cm\(^{-1}\) is attributed to residual S. The PS\(_4^{3−}\) ion, indicative of a glassy ionic conductor, has been reported at 420 cm\(^{-1}\). The 422 cm\(^{-1}\) peak attributed to FeS\(_2\) overlaps is superimposed with the PS\(_4^{3−}\) peak.

**Figure 4.** a) Schematic of the symmetric test cell used to measure the electronic conductivity of the (BM + HT + BM) sample. b) Schematic of the symmetric test cell used to measure the ionic conductivity of the (BM + HT + BM) sample. c) Cyclic voltammetry i-V curves at 25 °C and calculated electronic conductivity for the (BM + HT + BM) sample (solid blue) and a conventional control electrode with a composition dictated by Equation 2 (dashed blue). d) 10 mV DC polarization i curves for the same two electrodes at 25 °C (blue) and 60 °C (red). The stabilized current was used to calculate Ohmic ionic resistance in order to estimate ionic conductivity.
of capacity. An overcharge capacity of 114 mAh g⁻¹ indicates that 59% of the Li₂S added to the (BM + HT + BM) sample during the final ball milling step was electrochemically oxidized. We have previously reported on the electrochemical utilization of excess Li₂S in composite electrodes with the 22.5P₂S₅:77.5Li₂S glass electrolyte.²¹ In the prior study activation of excess capacity was correlated with the consumption of crystalline Li₂S, however, possible contributions to excess capacity from non-crystalline Li₂S was not ascertained. Even though the XRD spectra for (BM + HT + BM) does not indicate the presence of crystalline Li₂S it is reasonable that Li₂S may still be available for electrochemical utilization.

Assuming complete conversion of Equation 1, the (BM + HT + BM) electrode composite should theoretically only deliver 500 mAh g⁻¹ through the complete reduction of FeS₂. On the other hand, (BM + HT + BM) could also theoretically deliver 1024 mAh g⁻¹ assuming that no solid-state reactions occurred during electrode preparation and that the S and Li₂S precursors were fully utilized. On its initial discharge (cycle 2), the electrode delivers a specific discharge of 721 mAh g⁻¹. This discharge capacity, which is in between the two extreme values of 500 mAh g⁻¹ and 1024 mAh g⁻¹, provides further evidence for the complex composition of the (BM + HT + BM) composite electrode. The sweeping voltage profile between 2.4 – 1.9 V is attributed to the electrochemical reduction of residual S and of S created by the oxidation of excess of Li₂S during the initial overcharge. A small fraction of capacity may also be attributed to utilization of Li₂S in the glass electrolyte separator pellet.²¹ As expected, subsequent discharge profiles are much different than the initial discharge which indicates either a change in chemistry or kinetics.²¹,²³,²⁴ Quite impressively, the (BM + HT + BM) electrode delivers a specific energy density of 1,200 Wh kg⁻¹ (vs. Li⁺/Li). On its 40th cycle the (BM + HT + BM) electrode delivers a specific energy of 1,130 Wh kg⁻¹ (vs. Li⁺/Li), which attests to a good stability (Supporting Figure 2). The test cell provided in Figure 5 and Supplementary Figure 2 is included in this average. It is observed that the capacity of the (BM
+ HT + BM) electrode is not stable at higher rates. However, the capacity recovers when the current density is reduced. Figures 6b and 6c summarize the rate test for the cell presented in Figure 5. As the current density is increased, the lower voltage plateau, which we attribute to the reduction of FeS or an intermediary Li2-xFeS2 phase to Li2S and Fe0. As the current density is increased, the lower voltage plateau, which we attribute to the reduction of FeS or an intermediary Li2-xFeS2 phase to Li2S and Fe0.1,34–36 The lower plateau disappears because the kinetics of FeS or Li2-xFeS2 reduction may be limited by the solid state diffusion of Fe0 atoms needed to nucleate separate phases of Li2S and Fe0.

Discussion

The characterization of the (BM + HT) material yields data that does not support the formation of the glass former, P2S5. As mentioned, powder XRD peaks for crystalline P2S5 are absent and elemental mapping indicates that signals for P and S are segregated. The observation of FeP attests to the inadequacy of the proposed reaction mechanism. Nevertheless, the ionic conductivity and Raman spectroscopy of the (BM + HT + BM) electrode indicate the presence of an ionically conductive glassy electrolyte. Indeed, the ionic conductivity of the (BM + HT + BM) electrode was nearly double that of the convention control electrode with prepared glass electrolyte. Mechanochemical milling of (BM + HT) with Li2S will yield a material with a heavily altered structure that may include a glassy electrolyte. Powder XRD results indicated that the initial ball milling step did not induce a solid-state reaction, but the same may not be true for the second ball milling step. The reactivities of FeP, S and other possible unidentified reaction products under mechanochemical action are not known. Preparation of sulfide glass electrolytes without P2S5 as a precursor is not without precedent. The mechanochemistry of the (BM + HT + BM) sample should be performed to confirm the mixing of P and S signals. Unfortunately, this characterization was not completed due to a lack of resources.

Conclusions

We have demonstrated an electrode which delivers a specific energy of 1,200 Wh kg−1 which ranks it among the most energy dense all-solid-state electrodes to be reported. Even though our proposed reaction mechanism is incomplete it does provide a good starting framework for understanding the coincident preparation of FeS2 and glass electrolyte precursors. While the composition of the composite electrode is not yet well understood, its high performance suggests that much promise lies ahead for structuring interfaces via solid-state reactions.

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