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Transition Metal Polysulfides as Battery Cathodes

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ABSTRACT

Amorphous polysulfides of iron, nickel, and cobalt were prepared and characterized. The resulting compounds, Co_2S_7, Co_2S_9, Ni_2S_7, and Fe_3S_8 were evaluated as cathode materials in organic electrolyte lithium batteries. The cobalt compounds in particular delivered very high capacities of 1-1.2 A-h/g at voltages around 1.8V. The resulting cells possessed high gravimetric and volumetric energy densities.

Sulfur is a very high energy density cathode for a lithium battery. Since elemental sulfur is an extremely good insulator, it has poor properties as an electrode. Sulfur is also soluble in some organic solvents, and tends to form polysulfides which are even more soluble in the presence of an alkali metal sulfide. Thus, sulfur does not appear to be an attractive candidate material for use in an organic electrolyte ambient temperature lithium battery. Metal sulfides with a fully reduced sulfur, such as FeS, do not utilize the high energy density of sulfur, since the sulfur does not participate in the overall reaction [1]

$$2Li + FeS \rightarrow Li_2S + Fe \qquad [1]$$

Earlier workers have tried to utilize the high energy densities of sulfur by using alkali metal polysulfides. In one case, the lithium polysulfides were dissolved in a THF based organic electrolyte and discharged at a porous carbon electrode, giving a rechargeable cathode (1). Since both polysulfide species were soluble, both high rate discharge and recharge were expected [2]

$$Li_2S_4 + 2Li \rightarrow 2Li_2S_2 \qquad [2]$$

In another, more recent approach, the alkali metal polysulfides were used in electrolytes in which the polysulfides were insoluble. The resulting cells had a much longer storage life, but high current capabilities of the cells were limited (2). Both previous examples of polysulfide electrochemistry promised high gravimetric energy densities, but limitations on power capability and/or storage have, thus far, prevented commercial development of the systems.

A composite approach is to combine the very high energy density of sulfur with the insolubility and good electrochemical behavior of a transition metal sulfide. An excellent example of such a compound, which combines both sulfur capacity and sulfide cathode characteristics, is iron pyrite, FeS_2. The electrochemistry of iron pyrite has been studied and very high gravimetric and volumetric energy densities have been shown to be attainable (3). The discharge of FeS_2 is a complex process, unlike the simplified form [3] shown below, although this appears to approximate the final products and stoichiometry

$$FeS_2 + 4Li \rightarrow Fe + 2Li_2S \qquad [3]$$

There are numerous examples of transition metal disulfides to choose from, such as CoS_2, NiS_2, and MnS_2, as well as FeS_2. Metal trisulfides and higher sulfides are much less well known, with TiS_3 and VS_4 being the only well-known first row polysulfides and MoS_3 and NbS_3 in the second transition series. This is in substantial contrast to the alkali metals, where species such as Cs_2S_6 and Na_2S_5 are comparatively stable and well known. In view of the growing chemistry of polysulfide complexes from 1901 to the present, it appeared likely that other metal sulfides of higher content, analogous to $[Mo_2S_{12}^{-2}]$ and its congeners, might exist (4, 5). The possible existence of stable or metastable polysulfides of iron group metals was particularly interesting, because of the familiarity and stability of FeS_2, CoS_2, and NiS_2. We, therefore, attempted to prepare and characterize polysulfides of the iron triad (Group VIIIA) metals. The results of this investigation are reported below.

Experimental

There were no recent references in the literature to clearly characterized polysulfides of iron, nickel, or cobalt, although numerous references to disulfides of the iron triad (Group VIIIA) and to complexes involving these metals and sulfur or sulfides were found. A computer search of the earlier literature was not successful in clearly defining the earlier experience in the field either. A few references were found by a manual search of C.A., but most of the applicable work predated 1900. The most relevant papers relating to our own interest were those of Chesneau and Magrini (6, 7) to the polysulfides of cobalt and nickel, respectively. The older work was considered to be unreliable in the absence of any characterization, other than by elemental analysis of the products. It was therefore decided to begin with a screening procedure to determine whether any iron group polysulfides were stable at room temperature. The following preparations were developed from this screening procedure. In the screening procedure, a weighed sample of a soluble metal salt was dissolved in degassed distilled water and a stock sodium tetrasulfide solution was added. It was found that separation of product was much easier when a modest excess (*ca.* 10%) of the metal ion was present. When the polysulfide was in excess, an infiltrable black sludge was produced. The black products were stirred in solution overnight under argon and then vacuum filtered under argon to give a highly hydrated black solid. This black solid was vacuum dried at 60°C to remove water and was then analyzed by elemental analysis and DSC. The samples were then heated at 160°C under vacuum until sulfur evolution had ceased. The resulting black fine powder samples were then analyzed for sulfur and metal and subjected to powder diffraction and DSC measurements. From this initial screening the following preparations were developed.

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CoS_5.—Cobaltous sulfate hydrate ($CoSO_4$ $7H_2O$) (1*M*) was dissolved in deaerated, distilled water (1 liter) in a 3 liter, 3-necked r.b. flask equipped with an argon purge and a good mechanical stirrer. To the cobalt solution was added 0.9 mol of commercial 40% Na_2S_4 solution which had been saturated with sulfur and diluted with distilled deaerated water to 1 liter. The 40% Na_2S_4 solution is about 3*M* in concentration as received. The Na_2S_x (x = approx. 4.5 by our analysis) solution was slowly added to the cobalt sulfate solution through a dropping funnel over about a 2-3h period. It is useful to introduce the argon blanket through the funnel during this period. The solution becomes a thick black slurry and the mechanical stirrer must be used to provide good mixing. The resulting slurry is stirred for at least 48h under argon. During this time the slurry breaks up into a fine particulate powder and, if stirring ceases, will settle out slowly. The solid product is collected either by vacuum filtration, using a fine porosity fritted glass filter, or by centrifugation. The crude product is then washed free of soluble Co^{2+}, Na^+, and SO_4^{-2} with distilled water. If filtration is used to isolate the product, the maximum possible amount of water is removed under an argon blanket by use of the vacuum filter (commercial test papers for cobalt and sulfate are very useful in determining the progress of the washing operation). The crude product is then placed in a vacuum oven and dried at 60°C until no more water evolves. The result is an amorphous black solid of composition CoS_5. This material is air sensitive, especially above room temperature and decomposes to form cobalt sulfate and an acid product, presumably either sulfurous or sulfuric acid. A sample of material prepared in the same way, with cobalt acetate as cobalt source, contained small percentages of sulfate and, therefore, sulfate is the expected acid product. Found: Co 25.47; S 68.67; H_2O 2.93; Na 1.04. Theoretical Co 26.8; S 73.2.

Co_2S_7.—The preparation for CoS_5 is repeated, except that the stock Na_2S_4 solution is used in place of the sulfur saturated Na_2S_4. The crude black product from the vacuum drying is heated in the vacuum oven at 165°C, until no further sulfur is evolved. This gives a lumpy black powder which is extracted with toluene to remove any residual sulfur, leaving the finely divided black powder of Co_2S_7. If the heating process is carried out to completion in a good vacuum oven, there will be no sulfur remaining and very little oxidation to sulfate will occur. This material is somewhat air sensitive, especially with moisture and is kept in a sealed, argon filled container. Found Co 34.23; S 64.14. Theoretical Co 34.46; S 65.54.

Co_2S_9.—"CoS_5" is prepared by the procedure outlined above, except that the reaction mixture is stored for at least one week under argon before the filtering and initial drying. The crude product is vacuum dried at 165°C to give a fine black powder which analyzes as Co_2S_9 after toluene extraction. This material appears slightly more reactive than the Co_2S_7 and will give a smell of SO_2 especially when exposed to air at slightly above room temperature. Found: Co 28.50; S 70.63. Theoretical Co 29.01; S 70.99.

Ni_2S_7.—Nickel sulfate hydrate (1*M*) is dissolved in 1 liter of distilled water in a 3 liter flask, equipped with a mechanical stirrer and an argon purge. To this is added 0.5 mol Na_2S_4 solution in 0.5 liter water. The solution is added through a dropping funnel and stirred overnight under argon. The resulting black precipitate is collected under argon, washed fresh of the nickel excess with distilled water, and then vacuum dried at 60°C until all water is removed. The oven temperature is then increased to 150°C and the volatile sulfur is removed, leaving behind a black solid of Ni_2S_7. The nickel polysulfide is more air sensitive than either of the cobalt polysulfides. Found Ni 32.63; S 69.01. Theoretical Ni 34.3; S 65.7.

Fe_3S_8: ($Fe_2S_7 \cdot FeS$).—Ferrous sulfate (1*M*) is dissolved in 1 liter of degassed distilled water. The ferrous solution is placed in a 3 neck, 3 liter round bottom flask equipped with a mechanical stirrer and an argon purge. To this is added 0.5 mol Na_2S_4 stock solution diluted to 0.5 liter. The black slurry is stirred overnight and filtered under argon. The black solid is then washed with deaerated distilled water and vacuum dried, first at 60°C, then at 160°C to form a black, air-sensitive solid which analyzes as Fe_3S_8 (Fe 38.86, S 59.44; theory Fe 39.52, S 60.48). *Caution, the finely divided Fe_3S_8 may be pyrophoric.* The crude polysulfide described above may then be leached with 1*M* HCl to give Fe_2S_7. Found Fe 33.44; S 66.5. Theory Fe 3.25; S 66.75.

Electrochemical measurements were taken either with a PAR 173 Potentiostat equipped with a digital coulometer, or with a computer controlled battery test system. Thermal measurements were taken with a du Pont Differential Scanning Calorimeter. Elemental analyses were performed in-house.

A variety of test cells were used for electrochemical measurements on the metal polysulfide cathodes. Emphasis was placed on practical cell configurations which would permit testing in an electrolyte starved configuration and the use of cells with satisfactory sealing arrangements to permit real-time and accelerated storage tests on the polysulfide cells. A widely used package for initial testing was the foil laminate package. This is a prismatic cell of 4 to 2.5 cm rectangular electrodes sealed in an aluminized Mylar bag with from 2 to 4 cm^3 of electrolyte. This cell was easily adapted for reference electrode measurements by inserting a lithium reference electrode in the package as well. Such a cell was found to be suitable for elevated temperature storage tests, as well as initial testing. For foil laminate cells graphite 30%, PTFE 10%, and cathode material were carefully dried, then mixed with a blender inside an argon-filled glove box. The mix was then pressed onto a titanium grid to which a titanium tab had been spot welded. A typical cell has a cathode weight of 2g and an area (1 side) of 10 cm^2. Such a cathode is then assembled by heat sealing in a foil laminate package with a Li reference and Li anode, filled with an organic electrolyte (typically 70V/oPC; 30V/oDME; 1*M* $LiClO_4$), and then sealed. Typically a nonwoven polypropylene separator would be used to prevent shorting. Additional prototype cells were made using the ML950 coin cell and DL 2/3A wound cell configurations. The ML950 is a coin cell of 0.95 in. od and a capacity as a Li/MnO_2 cell of about 220 mAh, while the 2/3A is a spirally wound cylindrical cell equivalent in volume to an AA cell and having a capacity of about 1.2 Ah in the Li/MnO_2 chemistry. Both of these test vehicles used production cell tooling and were, thus, externally identical to production lithium cells.

Results

The elemental analyses of the polysulfides are in not in themselves convincing evidence for the existence of new phases, since the high sulfur compositions could be ascribed to poor sulfur extraction in either the drying or washing stages.

Thermal analysis of the dried crude polysulfide shows the sulfur melting at around 100°C and other, not easily assignable, thermal activity including a substantial endothermic transition, as shown in Fig. 1. Comparison with DSC curves of the known metal sulfide and disulfide indicated the presence of an uncharacterized phase. After exhaustive heating at 165°C under vacuum, the physical appearance of the product is not greatly changed but the thermogram shows that a profound change has occurred. This change in thermal behavior is correlated to the loss in sulfur during the vacuum drying operation. The resulting product is an extremely finely divided black powder. X-ray diffraction indicates an amorphous material with a diffuse absorbance pattern which is vaguely similar to the metal disulfide. SEM photomicrographs, as shown in Fig. 2, show a very finely divided powder with a particle size of from 0.1-0.3 μm. Although the particles themselves appear to be crystallites, it is possible that the apparently amorphous material is, in fact, too fine to give a good powder pattern. It is also possible that the apparent crystallites are either not crystalline at all, or else aggregates of even finer particles.

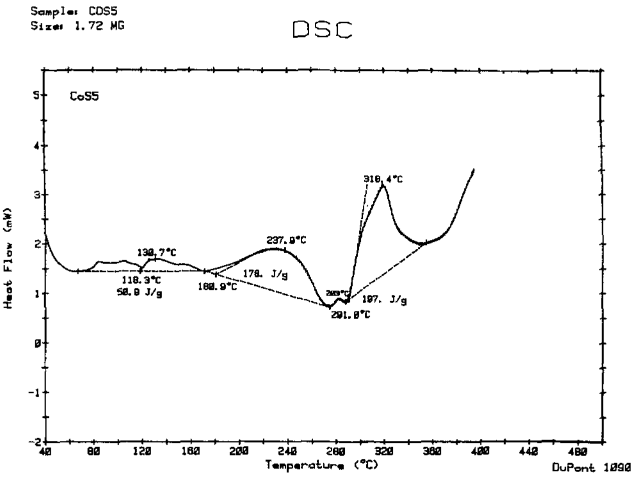

Fig. 1. Differential scanning calorimetry (DSC) analysis of the uncured cobalt polysulfide, CoS_5.

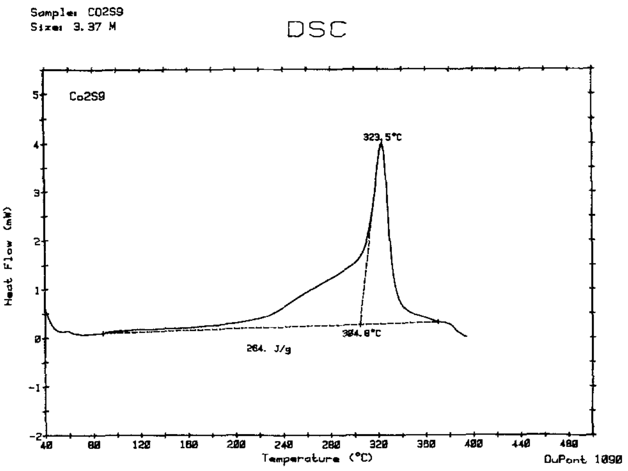

Fig. 3. DSC curve of vacuum cured cobalt polysulfide (Co_2S_9) showing the exothermic decomposition to S and CoS_2.

While the amorphous nature of the products is disappointing, it is not unusual, since the familiar polysulfide MoS_3 appears to be quite amorphous.

The cobalt polysulfide Co_2S_9 shows a density of about 2.8 by pycnometry in kerosene and an apparent density of 0.7 for the uncompressed powder. The density of Co_2S_7 was about 3.1, while the density of the other materials was not precisely determined but appeared to be in the same range as the cobalt compounds. The cobalt polysulfide materials show a DSC characterized by an exothermic decomposition near 280°C, as shown in Fig. 3. The absence of any endotherm due to elemental sulfur melting demonstrates that we are dealing with a true metal polysulfide, rather than an intimate mix of metal sulfide and sulfur, as might be argued from the elemental data alone. On a return scan to cooler temperatures, the solidification of sulfur is observed, showing that sulfur is formed in the exothermic process around 280°C. X-ray diffraction of the decomposed polysulfide shows that the metal disulfide is also formed and the decomposition reaction can thus be represented as [4]

$$Co_2S_7 \rightarrow 2CoS_2 + 3S \qquad [4]$$

While the cobalt polysulfides are nonconducting, the nickel equivalent is a good electrical conductor. The apparent stability of these materials to air varies from metal to metal, with Co_2S_7 appearing most stable, with no apparent reaction to air, and Fe_3S_8 most reactive, turning orange in moist air and easily burning in air. It is worth noting that the very early work of Chesneau appears essentially correct with regard to cobalt, although we cannot confirm the nickel results (6). Repeated experiments in our laboratories by different experimenters have shown a good degree of reproducibility in these preparations, indicating the formation of metastable transition metal polysulfide phases. Limited experimental data suggest that the sulfur content of the polysulfide and the metal/sulfide ratios have only a limited effect on the product composition, as does the cation in the polysulfide source. The crude products, before the 165°C drying process, vary more in sulfur content with higher alkali polysulfides, showing higher sulfur content in the products. After the vacuum heat-treatment, however, the metal sulfur ratios are independent of starting material and sulfur content, provided there was sufficient sulfur present. Cobalt and nickel sulfates are convenient starting materials although chlorides, bromides, nitrates, and acetates have also been used successfully.

The high sulfur content of these materials suggested that they could be usable solid cathode materials. Gravimetric capacity figures range from 1.0 Ah/g for Fe_3S_8 to 1.26 Ah/g for Co_2S_9, figures substantially higher than for almost all other cathode materials. These numbers are based on complete reduction of the polysulfide to the metal and assume reduction of any intermediate disulfide or sulfide product. When a volumetric basis is used, the figure of almost 3.4 Ah/cm^3 of cathode materials remains extremely high, based on the pycnometric density of the cobalt polysulfide powder. If extreme care is not taken in the preparation, a mixture of the 7 and 9 sulfur polysulfides is formed and the analysis is intermediate between those limits. At this time, we have no evidence of a stable polysulfide or polysulfides of cobalt with either a sulfur composition higher than $CoS_{4.5}$, or less than $CoS_{3.5}$, except for the well-known disulfide.

Cathode limited cells were prepared for the materials, Fe_3S_8, Co_2S_7, Co_2S_9, and Ni_2S_7 and discharged at low

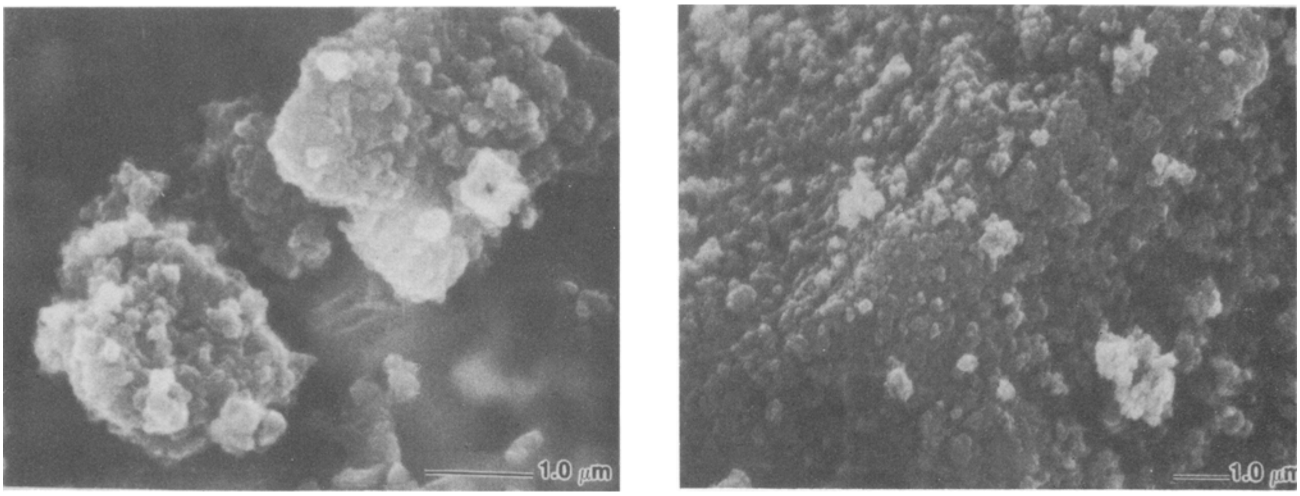

Fig. 2. SEM photomicrographs of cobalt polysulfide Co_2S_9

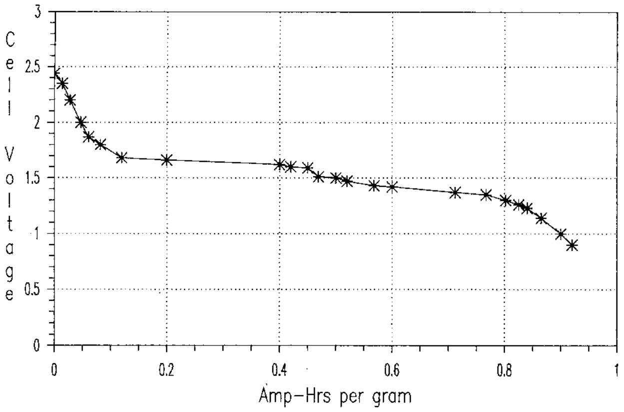

Fig. 4. Discharge curves of Fe_3S_8 in cathode limited cells at very low rates.

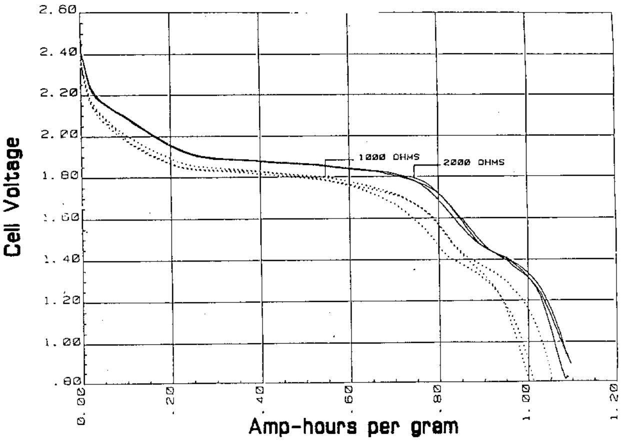

Fig. 6. Discharge curve of Co_2S_9 in cathode limited cells

rates. These low rate discharges are run at either a 1 or 2 kΩ load using a standard weight of 100 mg of polysulfide and, thus, take about a week to discharge. For ease of construction and handling, these cells were made in the ML950 coin cell hardware. This gasket sealed coin cell is about 0.95 in. external diam and has an electrode area of 3.16 cm^2. The resulting discharges, shown in Fig. 4-7, indicate the reasonable discharge voltage of 1.6-1.8V and high discharge capacity of over 1 Ah/g on the low rate discharge. The gravimetric energy densities found for the polysulfides, as well as volumetric energy densities, are listed in Table I. The molecular weights, theoretical formula equivalents, and theoretical specific capacities are also listed. The cobalt polysulfide, Co_2S_9, discharges in two apparent plateaus, as shown in Fig. 8, to give 2 and 5.5 Wh/cm^3, both of which are extremely high values. For comparison, MnO_2 in Li/MnO_2 cells gives about 0.9 and 4.2 Wh/cm^3. These high experimental energy densities on low current discharge appeared quite promising. These calculations are based on cathode alone. As one might expect, results with lithium included do not differentiate between cathode materials to the same extent. The high energy density and somewhat greater stability of the cobalt compounds lead us to select them for further evaluation. We prepared a series of foil laminate cells for higher current evaluation with results shown in Fig. 9. The good high current performance of the Co_2S_7 cathode is shown, even though the thick cathodes under test were not well suited to high current discharge. This continued rate limitation on our cells was shown by the absence of a linear region at low current in the plot of log i_d *vs.* specific capacity.

With the validity of our polysulfide concept established, we refined the preparation of Co_2S_7. Coin cells were made using available tooling for comparison with a realistic package and for capacity retention and storage at elevated temperatures. In Fig. 10, performance of a Li/MnO_2 coin cell and the CoS_x equivalent are shown on equivalent load, consisting of 1000Ω for the cobalt polysulfide cell and 2000Ω for the MnO_2 cell, allowing both cells to discharge for about the same time period. One year of real-time storage or up to 1 month of 60°C storage appeared to have no appreciable effect on the polysulfide cell capacity or voltage.

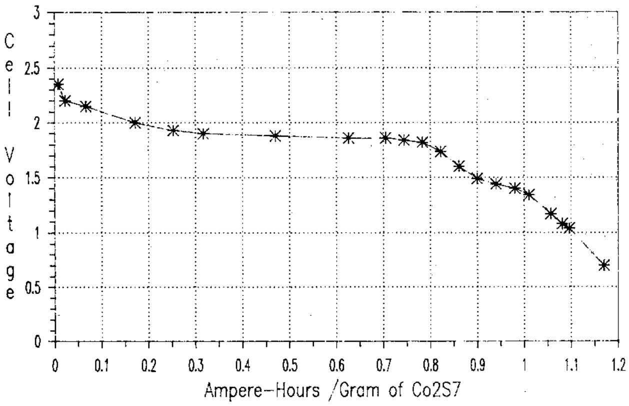

Fig. 5. Discharge curve of Co_2S_7 in a cathode limited cell. Indicated voltage is the average of three cells.

At this point, we decided to investigate the discharge process further. An x-ray study of a completely discharged cell revealed the presence of lithium sulfide and metallic cobalt. With indications of a second plateau in the discharge, we hypothesized that the discharge reactions were [5] and [6]

$$Co_2S_7 + 10Li \rightarrow 5Li_2S + 2CoS \qquad [5]$$

$$CoS + 2Li \rightarrow Li_2S + Co \qquad [6]$$

It appeared possible that a stepwise reduction of the polysulfide was occurring, as outlined in [7]

$$CoS_x + 2Li \rightarrow CoS_{x-1} + Li_2S \qquad [7]$$

As shown in Fig. 11, a plot of equivalents of charge *vs.* Co suggests the presence of second process at about 10 Li/Co_2S_7. This observation suggests that a continuous process occurs up to that point and that the final reduction to the metal itself is by a different discharge process than the major one taking place in the cell.

This mechanism suggested that cobalt polysulfide/lithium should not be rechargeable. In contrast, actual cells recharged reasonably well, as shown in Fig. 12, which shows the third discharge cycle for a foil laminate cell. As would be expected from the two stages of the discharge process, the rechargeability of the cathode is better, if not discharged below the first step. Poor behavior on extended cycling is due to use of an unsuitable cathode for secondary cell use, as well as lack of a sufficient lithium excess and use of an unsuitable electrolyte. However, the inherent rechargeability of the system is established. By analogy to $NbSe_3$ and MoS_3, as well as Mo_6Se_8, which demonstrate insertion of more than one lithium ion in a host structure without decomposition of the host, we suggest as an initial process [8] (9, 10)

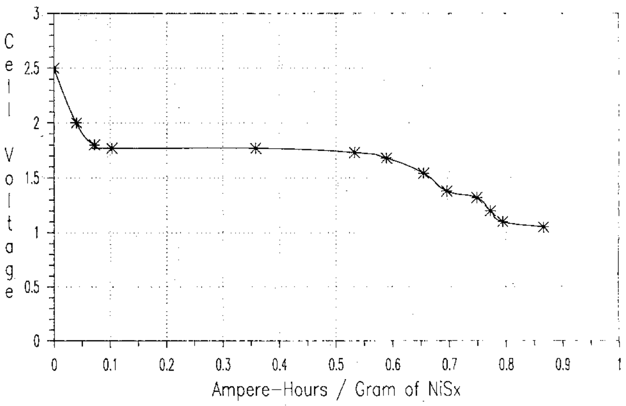

Fig. 7. Discharge curve for Ni_2S_7 in a cathode limited cell

Table I. Energy densities of Group VIIIA polysulfides

Material	M.W.	Density	Ah/g (calculated)	Ah/g (found)
Co_2S_9	405.8	2.8	1.189	1.15
Co_2S_7	341.8	3.1	1.098	1.05
Ni_2S_7	341.4	2.8	1.099	0.95
Fe_3S_8	423.55	2.7	1.012	0.95

Material	Ah/cm³ (calculated)	Ah/cm³ (found)	Wh/cm³ (found)
Co_2S_9	3.33	3.22	5.8
Co_2S_7	3.40	3.26	5.9
Ni_2S_7	3.08	2.66	4.5
Fe_3S_8	2.73	2.59	4.1

$$Co_2S_7 + 10Li \rightarrow Li_{10}Co_2S_7 \qquad [8]$$

This lithium insertion would be an essentially reversible process to give a partly lithiated cobalt compound. Further lithiation would then destroy the structure of the compound to give Li_2S and Co. Since our cobalt compounds appear amorphous and are insoluble in ordinary solvents, we use Co_2S_7 with the understanding that the actual formula could be much more complex, similar perhaps to the copper and molybdenum cluster anions (11, 12). We are pursuing efforts to prepare these materials in crystalline form, as well as other measurement techniques, to better characterize these compounds.

The crude polysulfide product is not particularly stable and slowly oxidizes in moist air to form $CoSO_4$, SO_2, and H_2SO_4. In contrast, the cured cobalt polysulfides appear more air-stable and are nonhygroscopic. The cobalt polysulfides are slightly soluble in HCl and dissolve in aqua regia forming some sulfur. Strong base also destroys the polysulfide, while weak or dilute acids and bases have no visible effect. A hydrated cobalt polysulfide has been reported earlier in the literature (6). This material was prepared by a generally similar method, reaction of polysulfide with an excess of a cobalt salt. The resulting product was a hydrate and it is unclear whether it corresponds exactly to our product or not. The preparative reaction for cobalt polysulfide is not straightforward, although a very simple reaction scheme can be written (9). Analysis of the supernatant liquid gives somewhat more sulfate than the equivalent amount of sodium and Co^{2+}, while the *p*H becomes more acidic, suggesting formation of HSO_4^-. The known tendency for polysulfides to form both thiosulfates and sulfates, as well as the sulfur liability between the different polysulfides, suggests the stability of the polysulfide is controlled by the metal, rather than the sulfur source used. It is at least possible that the initially formed polysulfides are chain polymers similar to alkali metal polysulfides and that heating causes a condensation to a ring type of compound with the polysulfide acting as a chelating ligand

$$Co^{2+}(SO_4^{-2}) + Na_2S_5 \rightarrow CoS_5 + Na_2SO_4$$

$$CoS_5 \rightarrow Co_2S_7 + 3S \qquad [9]$$

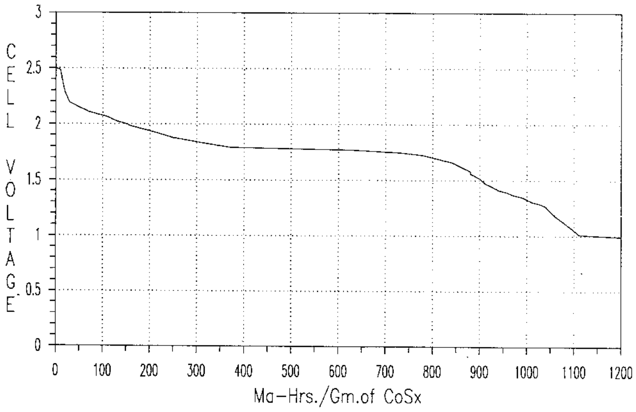

Fig. 8. Discharge of a cobalt polysulfide cell showing the second voltage plateau at about 1.4V.

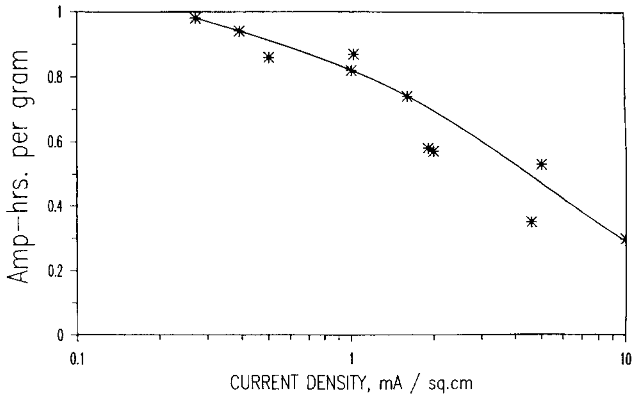

Fig. 9. Discharge of foil laminate cobalt polysulfide cells at different rates, showing the decline in utilization with increased current density.

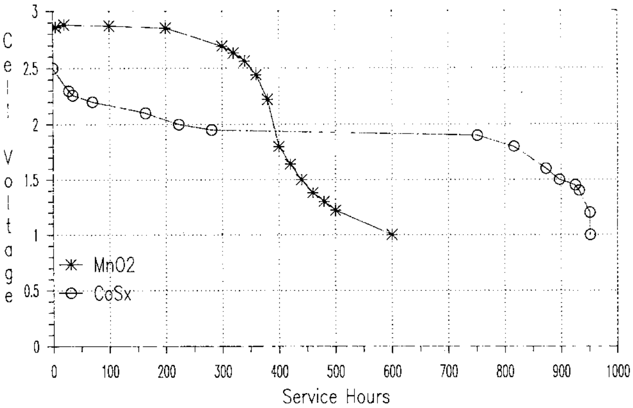

Fig. 10. Comparative discharge of cobalt polysulfide and manganese dioxide coin cells showing the increased energy of CoS_x.

We have also prepared similar polysulfides in nonaqueous solution by treating $CoCl_2$ with $[N(C_4H_9)_4]_2S_4$ in CH_3CN, forming an insoluble, as well as a soluble polysulfide species. This soluble species analyzes as (approximately) $N(C_4H_9)_4CoS_8$ and gives an NMR signal which suggests that at least some of the cobalt is present as Co (III). It is too early in the investigation to determine whether the behavior is similar to that observed by Holm in cobalt ethanedithiolates (11).

Both iron (II) and nickel (II) salts were treated in a similar manner, giving products roughly corresponding to the analyses Fe_3S_8 and Ni_2S_7. Since the iron product was somewhat soluble in 1*M* HCl, we prefer to formulate the products as FeS: Fe_2S_7, and Ni_2S_7. Both manganese, cop-

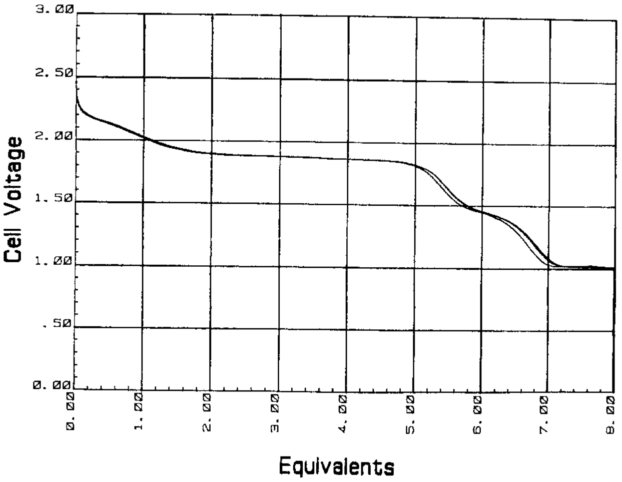

Fig. 11. Discharge of a cathode limited cobalt polysulfide cell (Co_2S_7), plotted to show the number of equivalents of charge transferred per cobalt at low rate.

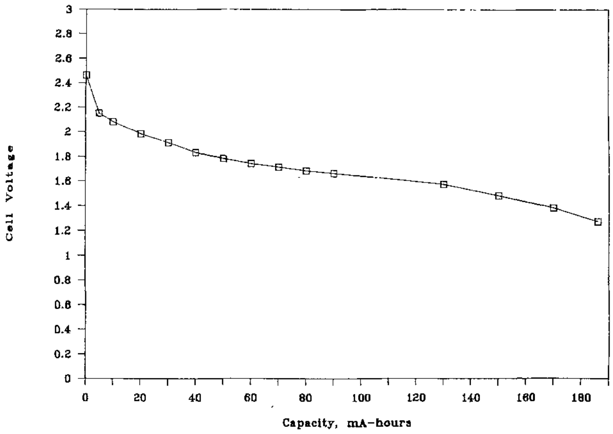

Fig. 12. Discharge of a cobalt polysulfide cell at 2 mA/cm² after two previous deep discharge and recharge cycles, showing the rechargeability of the system.

per, and zinc show somewhat different behavior with Mn and Zn giving orange brown products, while copper forms a copper (I) complex similar to NH_4CuS_4. In contrast to alkali metal polysulfides, the discharge potential varies with metal center and is below the 2+V for sulfur reduction alone. At the same time, the current capability is higher (10+ mA/cm² *vs.* 0.1 mA/cm²), than has been shown for alkali metal polysulfides, leading us to suspect that initial reduction takes place at the metal center. The metal centered reduction could then be followed by an intramolecular redox process in which the polysulfide would reoxidize the cobalt center [10]

$$Co_2(III)S_7 + 2Li \rightarrow [Li_2Co_2(II)S_7] \rightarrow Li_2Co_2(III)S_7 \qquad [10]$$

Conclusion

Amorphous polysulfides of iron, cobalt, and nickel were prepared by precipitation from aqueous solution followed by heating to remove water and pyrolyze the initially formed unstable product to a metastable species. The cobalt polysulfides were substantially less reactive than either iron or nickel and were evaluated as cathode materials in a lithium battery. The cobalt compounds proved to be high energy density cathode materials, delivering 1.1 Ah/g and 3.1 Ah/cm³ with 2 Wh/g and 5.5 Wh/cm³ on a theoretical and experimental basis. In practical cells the lithium CoS_x system delivers 225 Ah/kg and 400 Wh/kg on a gravimetric basis and 375 Ah/dm³ or 625 Wh/dm³ on a volumetric basis. On a theoretical basis, the cells should give very high energy densities of 900 Ah/kg or 1270 Ah/dm³. When lithium weights and volumes are included in this calculation, the values are 0.86 Ah/g or 1.54 Wh/g and on a volumetric basis 1.29 Ah/cm³ and 2.8 Wh/cm³. These energy densities are higher than many lithium battery systems.

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Performance Models for Zirconia Electrolyte Cells at Low Current Density

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ABSTRACT

This preliminary design study compares high temperature electrolysis, having $H_2O(g)$ flow delivered parallel to the tube (model 1), with $H_2O(g)$ reactant cross-fed, perpendicular to the axes of series-connected tubes (model 2). Calculations for model 1 correlate with relevant experimental data. Model 2 calculations predict higher energy efficiencies than model 1. If model 2 design philosophy is employed, hydrogen production is estimated, at 99.9% purity, and at 100 mA/cm², to require 1.017V at 0.902 energy efficiency, using tubular cells employing the present design. Tube design optimization, with normalized cell resistance, ρ lowered to 0.35 Ω cm², is estimated to result in 99.9% pure hydrogen product at 0.952V and 0.963 energy efficiency for the same 100 mA/cm² design point. Hydrogen purity, cell current density, and resistance are key modeling parameters.

An electrical generator employing a low temperature hydrogen-oxygen fuel cell in closed cycle with a high temperature H_2O electrolysis cell with solid oxide electrolyte (*e.g.*, 1000°C) will provide a net power output (P_{net}) if sustaining solar thermal energy is available and cell current efficiencies, α'_f and α'_e are high. If V_f and V_e are, respectively, fuel cell and electrolysis cell driving voltages, then, at a current, I

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