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DE82 005392

AC03-76SF90363

ANNUAL REPORT/E-4

"SYNTHESIS AND EVALUATION OF NEW CATHODE MATERIALS FOR RECHARGEABLE LITHIUM BATTERIES"

Contract No. EY-76-C-03-1253

Reporting Period: April 26 - 1976
to September 15 - 1977

E. C. Report No. 5.223
(S-3137)

December 1977

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Annual Report

SYNTHESIS AND EVALUATION OF NEW CATHODE MATERIALS FOR RECHARGEABLE LITHIUM BATTERIES

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1.0 ABSTRACT

The objective of the first year of this study was the investigation of two new classes of complex sulfide materials of potential value for ambient and high temperature, high energy rechargeable batteries with lithium anodes. The two new classes were the sulfospinels and simple and mixed layered disulfides of transition metals of groups IVB and VB. In addition, three simple sulfides, CoS, CoS_2 and FeS_2 were also investigated. Studies of the synthesis methods have resulted in the development of the two-zone quartz furnace capable of firing temperatures up to 1000°C with controllable sulfur vapor pressures. Optimum synthesis methods for preparation of TiS_2 and substituted disulfides of the type $M_xTi_{1-x}S_2$ (M = Co, Cr., Mo, V) as well as for sulfospinels have been established.

In the area of mixed disulfides, compounds with 5 mole % molybdenum and 25 mole % chromium or vanadium were found to be superior in electrochemical cell performance to TiS_2. The higher electrical conductivity of these compounds compared to that of TiS_2 is the probable reason. The preparation of the Co-substituted disulfide was not successful and resulted in a sulfospinel structure of $CoTi_2S_4$. Among the sulfospinels studied $CoCo_2S_4$ = (Co_3S_4) and $CoFe_2S_4$, high capacity densities up to 605 mAH/g have been found with the former showing more electrochemical reversibility. The cycling ability was found to be related to the depth of discharge in these initial studies. The mixed disulfides, and under proper conditions, the sulfospinels represent very promising cathode materials for rechargeable lithium cells. The initial findings in organic electrolyte cells have also been confirmed in high temperature tests conducted at Argonne National Laboratory in molten salt cell tests. The simple sulfides have been found to perform in organic electrolyte cells with CoS_2 showing lower pplarization than FeS_2 or CoS. Recommendations for future work include crystalographic studies of the new structures, further improvements in the techniques of synthesis, of cathode structure, and development of organic electrolytes.

2.0 INTRODUCTION

In the course of self-sponsored work, prior to this contract, the staff of Electrochimica Corporation has developed two classes of cathode materials of potential great interest for ambient as well as high temperature high energy rechargeable batteries employing lithium anodes. These two classes are the sulfospinels of the general formula $M^{I}M^{II}_{2}S_{4}$ and the certain layered dichalcogenides of transition metals of group IV and VB of the general formula MS_2.

The objective of the first half of this work, phase I, was an investigation of preparative techniques for these materials and their initial evaluation as cathodes for rechargeable lithium cells. The objectives of the second part, phase II, were the further synthesis studies and evaluation as cathodes of three simple transition metals: sulfides, three sulfospinels, and two or more disulfides, preparation of sulfide for high temperature cells, and literature search.

Following a brief initial literature search, certain methods of sjnthesis have been analysed and experimentally explored. Materials have been prepared and evaluated in experimental cells for electrochemical parameters and in complete cells for initial cycling performance. In addition, samples of cathode materials were prepared for evaluation in high temperature cell vs Li (Al) anodes with KCl-LiCl fused salt electrolyte at Argonne National Laboratory.

Among the simple transition metal sulfides, CoS, and the pyrites CoS_2, FeS_2, were briefly investigated.

This report concentrates on the first contractual efforts to synthesize and initially evaluate the two promising classes of cathodic materials, namely: sulfospinels and layered transition metal disulfides.

3.0 TECHNICAL BACKGROUND

3.1 Selection Criteria for Desirable Cathode Materials

In order for a rechargeable battery system to perform satisfactorily over an appreciable number of cycles, there are three types of reversibilities which must be satisfied. These include physiochemical reversibility of all solid and liquid phases, morphological and crystallographic reversibility between the charged and discharged states of the active electrode materials and electrode kinetic near-reversibility as a basis for high rate capabilities without excessive polarization losses.

A desirable cathode material must be:

a) Stable in the electrolyte.

b) Essentially insoluble in the electrolyte (except as to the extent desirable from electrode kinetic considerations).

c) Should be electrochemically active (high current density capability without excessive polarization).

d) Should have a crystallographic structure conducive to morphological reproducibility as cycling proceeds.

The last consideration would indicate the desirability of a well defined crystallographic form for the cathode material. Additionally, a crystallographic form which encourages interaction exchanges between ions in the different types of sites is likely to give the material semi-conducting or even conducting properties, features much desirable to reduce internal ohmic drops and consequently the effective polarization of porous cathodes.

In its prior work the staff of Electrochimica Corporation has found that certain sulfide compounds namely belonging to groups which can be described as sulfospinels (ortospinels) and certain layered dichalcogenides offer a unique opportunity to meet most of the above criteria for desirable cathode materials*. These two classes are

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*Subject to patent applications by Electrochimica Corporation.

briefly discussed in the following.

3.2 The Sulfospinels

The sulfospinels (or selenospinels) are chalcogenide compounds generally analogous to the face-centered cubic crystal spinels and ferrites. They have a general formula

$$M_1^{II}M_2^{III}X_4$$

where X = S, Se, Te
M_1= divalent ions of Cu, Fe, Co, Ni, MnZn
M_2= trivalent ions of Ti, V, Cr, Fe, Co Ni

In a unit cell (containing 32X) of a normal spinel the divalent M_1 ions occupy only 8 out of the available 64 tetrahedral positions. The trivalent M_2 ions occupy 16 out of the available 32 octahedral positions. This means that in the lattice there are many vacancies, especially in the tetrahedral type for introduction of lithium ions during the discharge react on at the cathode in a cell. This is considered to be the fundamental attraction of the sulfospinel group. These compounds offer the great variety of chemical substitutions for both cations and anions.

The cobaltites $M_1Co_2S_4$ and the chromites $M_1Cr_2S_4$ have clearly been established as "normal" spinels; i.e., in which the metal ions M_1 occupy only tetrahedral positions. The magnetic properties of these compounds have been studied extensively by Lotgering (1).

On the other hand, it appears that the ternary chalcogenides of titanium of the general formula MTi_2S_4 (M = Fe, Co, Ni) do not have a spinel structure and instead exhibit a monoclinic Cr_3S_4-type structure which is characterized by ordered vacancies in alternate metal layers. (2) Wold and co-workers (2) have found for both sulfides and selenides of this type that such compounds will sometimes undergo a transition to the disordered trigonal structure if there are deviations from the stoichiometry MTi_2X_4.

Since it is important in battery work to reduce the weight of the active materials, the present primary interest in this program is on the sulfur compounds. These compounds are generally metallic conductors (resistivity in the range 10^{-2} - 10^{-4} ohm-cm). They have positive temperature coefficients of the resistivities and low Seebeck efficiencies (approximately 10 μ volts/°). Lotgering (3) was one of the first to study a series of these compounds because of their interest in the magnetic applications field. He developed some synthetic methods limited, however, to very small quantities.

3.3. Layered Dichalcogenides

Another interesting class of compounds are the layered dichalcogenides of the transition elements of columns IV and VB and their intercalation complexes. These compounds have recently been extensively studied because of emphasis on their super conducting properties (4). The layers of the crystals are separated in the Van der Walls gap by inorganic species intercalated between the dichalcogenide layers. For instance, TiS_2 has been described as a semi-conductor with a 1-eV gap. It shows a high metallic conductivity which is explained in terms of metal-rich off stoichiometry and degenerate semi-conductivity. The disulfides and diselendies of tantalum Ta, V and Cr have also been studied. The mixed disulfides; e.g., $Ti_{1-x}V_xS_2$ show high electric conductivity (resistivity in the order of 10^{-5} ohm-cm).

Several compounds in this class have recently been demonstrated as promising cathode materials; e.g., niobium di & tri-selenides (5), and TiS_2 (6). These materials operate by intercalation of lithium upon cathodic discharge between the layers of sulfur in the layered structure. For instance, the discharge of TiS_2 proceeds in accordance with the reaction

$$TiS_2 + x\,Li^+ + x\,\bar{e} \longrightarrow Li_xTiS_2$$

where $x = 0 \longrightarrow 1.0$

The reverse action occurs upon charging. When these processes occur reversibly in both directions the basis for a long life rechargeable battery system is provided. Since intercalation between the sulfur layers held together by weak Van der Walls' forces does not involve breaking of strong bonds the basis for reversibility is provided.

One of the early investigations at Electrochimica Corporation concerned mixed cations, dichalcogenides, or disulfides with an eye towards increasing substantially the intrinsic conductivity of the cathode materials and, therefore, of the practical electrodes. It has been found, for instance, that by substitution in titanium disulfide some of the Ti by a metal of group VB such as vanadium or by metals of group VIB such as chromium and molybdenum substantial increases in conductivity can be obtained. At first these were observed by noticing a considerable decrease in required charging voltages for cells with such cathodes. In other words, cathodes of this type polarize less for the same current density (See experimental examples illustrated further on). Supporting information was subsequently found in the literature (See e.g. 7) in contrast with the degenerate semi-conductivity of TiS_2 the mixed cation materials exhibit resistivities of the order of 10^{-3} ohm-cm at room temperature. The effect of the substitution of vanadium or chromium atoms for titanium atoms in the TiS_2 structure is to confer properties of a paramagnetic (or ferrimagnetic) metal on the system. The substitution of vanadium for titanium in the lattice has changed the electrical characteristics from that of a degenerate semiconductor in TiS_2 to metallic conductivity. Increases in conductivity by a factor of 2.5 have been reported (7).

Thus, the mixed cation disulfides represent a particularly intriguing group of materials exhibiting metallic conductivity on the one hand and operating as a cathode through intercalation of the small lithium ions without disruption of the lattice as charge, discharge proceeds.

3.4 Pyritic Metal Sulfides

A simple class of transition metal disulfides are the pyrites containing S_2 - units in which the S-S distance is almost exactly equal to that of a single S-S bond. The pyrites have a face centered cubic distorted NaCl structure in which the metal occupies the Na-position and the centers of the S_2 groups are placed at the Cl-position, but turned in such a way that they are not parallel to axes of the cube. The lattice constant a is 5.535 Å for CoS_2 and 5.418 Å for FeS_2(8).

Iron pyrite FeS_2 would be very attractive because of a theo. energy density of 1300 WH/kg (and a practical of 200-250 WH/kg) It has of course been the subject of considerable studies at Argonne N. L. in the molten salt electrolyte battery using LiCl-KCl sustems. In this system the reduction of FeS_2 goes through several solid phases, including $2Li_2S \cdot FeS \cdot FeS_2$ and $Li_2S \cdot FeS$. Whether such phases would also occur in an ambient temperature organic electrolyte battery is one question which would need to be considered from many points of view, including that of the thermodynamic stability for each of the phases. The two pyrites included in this study were FeS_2 and CoS_2. These two compounds belong to a series of transition metal dichalcogenides of the series 3d metals which occur often as minerals. FeS_2 has semiconductor properties with a resistivity of 2 x 10^{-4} ohm-cm (8). This different conductivity was expected to manifest itself in differences in the polarization of the two electrodes, both on charge and on discharge, especially at higher current densities.

4.0 EXPERIMENTAL WORK AND RESULTS

4.1 Synthesis Studies for Cathode Materials

Early in this work on the basis of an initial survey, it was determined that the methods for synthesis of transition metal sulfides, layered disulfides, and of sulfospinels (studied originally as magnetic materials) involved preparations from elements or by reaction of hydrogen sulfide with either metal chloride or with the elements. Many of these methods while suitable for one material are quire unsuitable for others. Thus, preparation of TiS_2, which in our program is an important intermediate for preparation of mixed layered disulfides, or for certain sulfospinels requires a very careful preparation by sulfur vapor transport to titanium metal in suitable form. Initially in the program, commercial grades of TiS_2 generally prepared by H_2S reaction with metal chlorides were obtained from Cerac, Inc., and from Great Western Inorganic Co. These materials were used both directly as cathode materials for evaluation in cells and as components in the synthesis of the more complex sulfides.

Our own efforts to synthesize TiS_2 were initiated according to method A from the elements. An initial effort involved pressing titanium metal powder and sulfur in stoichiometric ratios into pellets to achieve intimate contact and firing these in sealed quartz ampules. However, the tremendous exothermic heat readily caused fractures of the ampules. This led to the decision to avoid closed systems and to the design of a new apparatus which could be used either as a closed or as an open system which would provide for two heating zones so that the reaction can be moderated and readily controlled, by providing a reliable vapor pressure control for the transport of sulfur (9). In this new approach a vertical glass apparatus is used with a round bottom flask holding the sulfur at temperature 350 to 470°C (depending on the desired sulfur vapor pressure) and the reacting metals or sulfides are held in a glass basket suspended in a mid point of the upper cylindrical portion of the vertical furnace which can be heated separately to temperatures ranging from 500° to 750°C. Further improvements in this proceedure were achieved by the following modifications.

1. Introduce diamond cuts in both the bucket and the liner holding the reacting materials in the hot zone to facilitate ready access of sulfur vapor.
2. Provide a deep thermocouple well to permit accurate temperature measurement and control in the hot zone close to the bucket containing the reacting material.
3. Building the entire equipment from quartz to permit operation up to 100 °C.
4. Increasing the cool zone section to permit better gasket seals.

After the successful operation of this furnace, an identical second was set up to permit an enlarged scope of material syntheses. In each furnace firings involving 40 to 100 grams of mataerial could readily be made. This represents a very significant advance from the cool zone sealed long ampule method in which typically amounts of the order of 2-4 grams are prepared. The furnaces prove themselves capable of synthesizing both sulfospinels and layered disulfides. The most important task became the determination of the desirable time-temperature profiles and the number of firings necessary to complete the reaction.

From a variety of such studies, the following guidelines were learned.

1. TiS_2 and layered disulfides are best synthesized in the temperature range of 5 - 600°C. The differential with the sulfur generating zone should be of the order of 60 to 100.
2. Sulfospinels are best synthesized in the range of 650-850°C with a 2-400°C differential to the sulfa zone temperature.
3. The synthesis of mixed layered disulfides is best achieved by starting with TiS_2 and synthesizing it with stoichiometric additions of the appropriate metal elements and of sulfur.
4. 2 or 3 firings are usually desirable to achieve high yields of the desired compounds (over 90%).
5. The particle size and the reacting space is very important,

e.g., for titanium sponge a size range of -8 + 35 appears optimal.

6. Thorough elimination of air is critical during firings.

4.2 Cell Evaluation Studies

In order to permit an initial evaluation of a large number of materials resulting from various compositions and preparative techniques as well as the evaluation of different electrolytes, it was decided that cells should be sealed in such a way that they can be reliably tested in the normal laboratory environment, without requiring a dry box during the test stage. To accomplish this a sealed crimped cylindrical cell structure (C size) developed by Elca Battery Company, subsidiary of Electrochimica Corporation, was adopted with some modifications. The main change was to employ only a 5" long cathode instead of the usual 10". This provided for easier assembly and greater flexibility in the use of separators.

Cathode mixtures containing 20% graphite and 10% teflon were pressed to an expanded nickel grid 1.35" wide x 5" long. The anodes of the same width were 6" long and also supported on nickel grids. The separators were non-woven polypropylene on the electrodes and microporous polypropylene film as a barrier material. The electrode separator assembly in a coil form was placed in a C-cell can with appropriate insulators filled with the electrolyte and crimped with a polyethylene gasket. The cover of the cell was equipped with a nickel diaphragm type safety vent designed to release gas at a pressure of 30-40 psig. After the crimping operation the cells were removed from the dry box, cleaned and equipped with welded nickel tabs for electrical connections. In each group typically representing a given cathode material and electrolyte combination three cells were constructed. The data presented give a range of values for that group or an average when the data is reasonably close together (usually within a 10% bond).

In the first study a number of electrolytes were formulated on the basis of prior experience with rechargeable organic electrolyte type cells. The electrolyte compositions are given in Table 1. Since

TABLE 1

ORGANIC ELECTROLYTE COMPOSITIONS

El. No.	Solute m/L	Solvent
15c/2	1.2 $LiAlCl_4$	MCF
91/5	2.5 $LiClO_4$ 1.0 SO_2	70% THF + 30% DME
35/5	0.6 $N.Bu_4I$ 1.0 $LiClO_4$	40%PC - 60% THF
90/5	2.0 $LiAsF_6$	20% PC - 80% THF
92/5	2.5 $LiClO_4$ 1.0 SO_2	MCF
93/5	1.2 $LiClO_4$	MCF
94/5	1.2 $LiClO_4$ 0.5 SO_2	MCF
95/5	2.0 $LiClO_4$ 0.5 SO_2	70% THF - 30% DME

MCF = Methyl Chloroformate

THF = Tetrahydrofuran

PC = Propylene Carbonate

DME = 1.2 dimethoxyethane

the choice of the electrolyte and particularly of the anode can be critical for the performance of a secondary cell, we considered the evaluation of electrolytes to be an important initial task and therefore, endeavored to test several electrolytes with a given cathode. One good preliminary cathode vehicle for that purpose was considered" the cupric sulfide cathode which is known to be capable of rechargeability although to a limited number of cycles. The study of such cathodes with four different electrolytes is given in Table 2.

Judging from capacity delivered and charged-in and as well as voltage limits, the following tentative conclusions can be made:

1. Electroyyte 35/5 shows clearly the poorest results (on charge 3C with an input of only 556 mA cells reached 5-9 volts, when solvent would surely decompose.)
2. Electrolyte 92/5 failed to deliver good cell capacity in Step 2D. It also yielded lower voltage plateaus.
3. On the basis of these initial results electrolytes 90/5 and 91/5 appeared to be roughly comparable.

A solid solution of CoS and TiS_2 prepared by Great Western Inorganic under the instructions of Electrochimica Corporation, as indicated previously, showed a promising behavior from the outset. A new group of three cells was therefore constructed using electrolyte No. 95/5. (See Table 1) This group has given remarkably good results as shown in Table 3. The cells were discharged at rates ranging from a 20 hour rate to as fast as a 4 hour rate in various cycles. Table 3 shows the capacity outputs and inputs with the corresponding end voltages which, of course, are determining for those capacitities. Accordingly, capacities do vary from cycle to cycle and therefore it is more valuable to take an average for an entire group of cycles. These averages are a capacity output of 373 and an input of 485 mAH, corresponding to an average current efficiency of 76.9% for the first 16 cycles.

While historically the studies on cathode materials were initiated with preparations of sulfospinels and of disulfides and their evaluations

TABLE 2 - INITIAL EVALUATION OF ELECTROLYTES

Gp. No.	Cathode	El-yte	Disch/Charge Step	V_{in}	V_{av}	V_{fin}	mAH out	mAH in	Notes
27-4-1	CuS	90/5	1D (30 mA)	3.10	1.5-1.9	1.54	1110		
			2C (20 mA)	1.83	2.5	2.74		1585	
			2D (20 mA)	2.17	1.65	1.35	1110		
			3C (30 mA)		2.3	2.38		1386	
-2	"	91/5	1D (30 mA)	3.29	1.9	1.46	1110		
			2C (20 mA)	1.93	2.27	3.58		1585	
			2D (20 mA)	2.45	1.72	1.18	1110		
			3C (30 mA)		2.29	2.29		1386	
-3	"	92/5	1D (30 mA)	2.98	1.63	1.24	1110		
			2C (20 mA)	2.42	3.18	3.27		1585	
			2D (20 mA)	1.68		0.92	458		
			3C (20 mA)	2.46		2.27		1386	
-4	"	35/5	1D (30 mA)	2.8-2.57	1.5-1.7	1.0	400-630		
			2C (20 mA)	2.54	2.8	4-5		530-596	
			2D (20 mA)	1.87		1.14	320-458		
			3C (30 mA)	2.13		5-9		556	

TABLE 3

INITIAL D-SCANS FOR CoS & CoS_2 in EL-YTE 95/5 (Gp. 41-35;36)

Cell EMF's

C.D. mA/cm^2	CoS	CoS_2
0.25	2.5 v.	2.52 v.
0.5	2.42 v.	2.38 v.
0.75	2.30 v.	2.16 v.
1.00	2.08 v.	1.90 v.
1.25	1.84 v.	1.64 v.
Charge End-Volt. at 0.25 mA/m^2	3.15 v.	2.70 v.
Cap. to 1.1 V.	290 mAH/g =0.983$\bar{e}$/mole	290 mAH/g =1.33$\bar{e}$/mole

TABLE 4

INITIAL D-SCANS FOR FeS_2 in 3 ELECTROLYTES (Gp. 41-32)

Cell EMF's

C.D. mA/cm^2	95/5	03/6	06/6
0.25	2.22 v.	2.05 v.	2.54 v.
0.50	2.15 v.	1.88 v.	2.49 v.
0.75	2.04 v.	1.68 v.	2.44 v.
1.00	1.64 v.	1.48 v.	2.36 v.
Charge End-V. at 0.25 mA/^{2}	2.84 v.	2.82 v.	3.29 v.
Cap. to 1.1 v.	230 mAH/g =102$\bar{e}$/mole	-	-

were the first, a study of simple metal sulfides was added on the request of the technical monitor at midpoint during the program. It may, therefore, be desirable to arrange the discussion of these studies in the following three subsections.

4.2.1 Study of Simple Transition Metal Sulfides

This study included three compounds CoS and two pyritic compounds CoS_2 and FeS_2. The first two compounds were obtained from Cerac, Inc. and FeS_2 from Argonne National Laboratory. The latter is the same pyrite material as used in the high temperature battery cells being developed at Argonne. This material is purified only by a flotation method to remove silica. Table 3 shows initial discharge scans for CoS_2 cathods in lithium cells with electrolyte 95/5. This perchlorate electrolyte in a tetrahydrofuran-dimethoxyethane (THF-DME) electrolyte was used in almost all studies unless otherwise mentioned. The initial polarization of the pyrite CoS_2 would appear to be larger than that of the simple sulfide CoS. However, as seen at the bottom of Table 3, CoS_2 delivered 1.33 electrons per mole compared to .98 for the simple sulfide to the same 1.1 of cutoff. However, the capacity yield per gram was identical. CoS_2 shows acceptance of charge at the lower voltage as indicated by its lower voltage endpoint upon charging.

A comparison with FeS_2 can be seen in the first column of Table 4. In the same electrolyte FeS_2 at the same levels of current density, the lower cell EMF's were obtained. The capacity yield to 1.1 volts was only 230 mAH/g which is equivalent to 1.02 electrons/mole. The charge end voltage is close to that of CoS_2 pyrite. In a different kind of study, these three sulfides were compared with two substituted TiS_2 using a series of glass cells in which the cathode 1 in. x 1 in. in size was placed between two lithium anodes in a relatively large quantity of electrolyte, and the potentials were measured between the cathode and an unpolarized lithium referenced electrode in a side walled component connected to the lithium anode through a small Luggin capillary. Some difficulties occur with this experimental approach with the poor adhesion of the cathode material to the supporting nickel grids. Consequently, the work was limited to the initial two to three cycles. As shown in Table 5, for the original cathodes, the cathodic (or discharge) potential was lower for FeS_2 than for CoS_2, and all of the simple sulfides were lower than the cobalt substituted TiS_2. In this experiment all of the cathodes showed excessively large anodic (charge) potentials for the sulfide cathodes. At the end of a substantial discharge equivalent to 465 mAH/g, the highest cathodic potentials were obtained for CoS_2 and the $Co_{.25}Ti_{.75}S_2$. It is possible that this discharge was destructive of most of the materials except CoS_2 since the subsequent anodic potentials after charging in only 50 mAH/g were in the vicinity of a 4 volts or more. It should also be noted that of the last two substituted disulfides the one with composition $Co_{.25}$ behaved better both on charge and discharge.

The pyrite materials were the subject of further studies on which preliminary results were published. (10)

These two compounds belong to a series of transition metal dichalcogenides of the series 3d metals which occur often as minerals.

FeS_2 has semi-conductor properties and has a resistivity of 1.74 ohm-cm. On the other hand, CoS_2 is metallic and with a resistivity of 2×10^{-4} ohm-cm (8)ference 1).

This further study was conducted in the glass cells previously described using 1 in. x 1 in. cathodes.

Figure 1 shows a partial discharge and charge of a cell with CoS_2 and Figure 2, a similar one for FeS_2. The discharge plateaus are variable in both cases. The lower plateau for CoS_2 is about 1.54 volts and for FeS_2, 1.44 volts. In Figure 2 we see what may amount to three charging plateaus. The highest one is probably due to solvent oxidation at the high voltage. No effort has been made to illustrate the reaction details at this point. An interesting comparison of the two pyrites is shown both for cathodic discharge and for anodic charge in the form of Tafel plots

TABLE 5

END POTENTIALS OF 5 CATHODE MATERIALS VS. Li-REF (G. 71 thru 75)

Glass Cell Study

	C.D. mA/cm^2	FeS_2	CoS_2	CoS	$Co_{.33}Ti_{.66}S_2$	$Co_{.25}Ti_{.75}S_2$
For orig. charged Cathodes						
Cathodic (disch.)	2	2.00v	2.25v	2.05v	2.31v	2.26v
Anodic (charge)	2	3.8	3.89	3.56	3.72	3.73
Cathodic after init. disch. (ID) of 465 mAH/g	1	0.13	1.27	1.18	0.57	1.35
Anodic after charge (IC) of 50 mAH/g	1	(4.3)	3.50	4.06	4.12	3.98
Cathodic after disch. (2D) of 140 mAH/g	1	-	1.11	0.99	0.49	1.11

FIG. 1 TYPICAL CYCLE FOR CoS_2-Li CELL

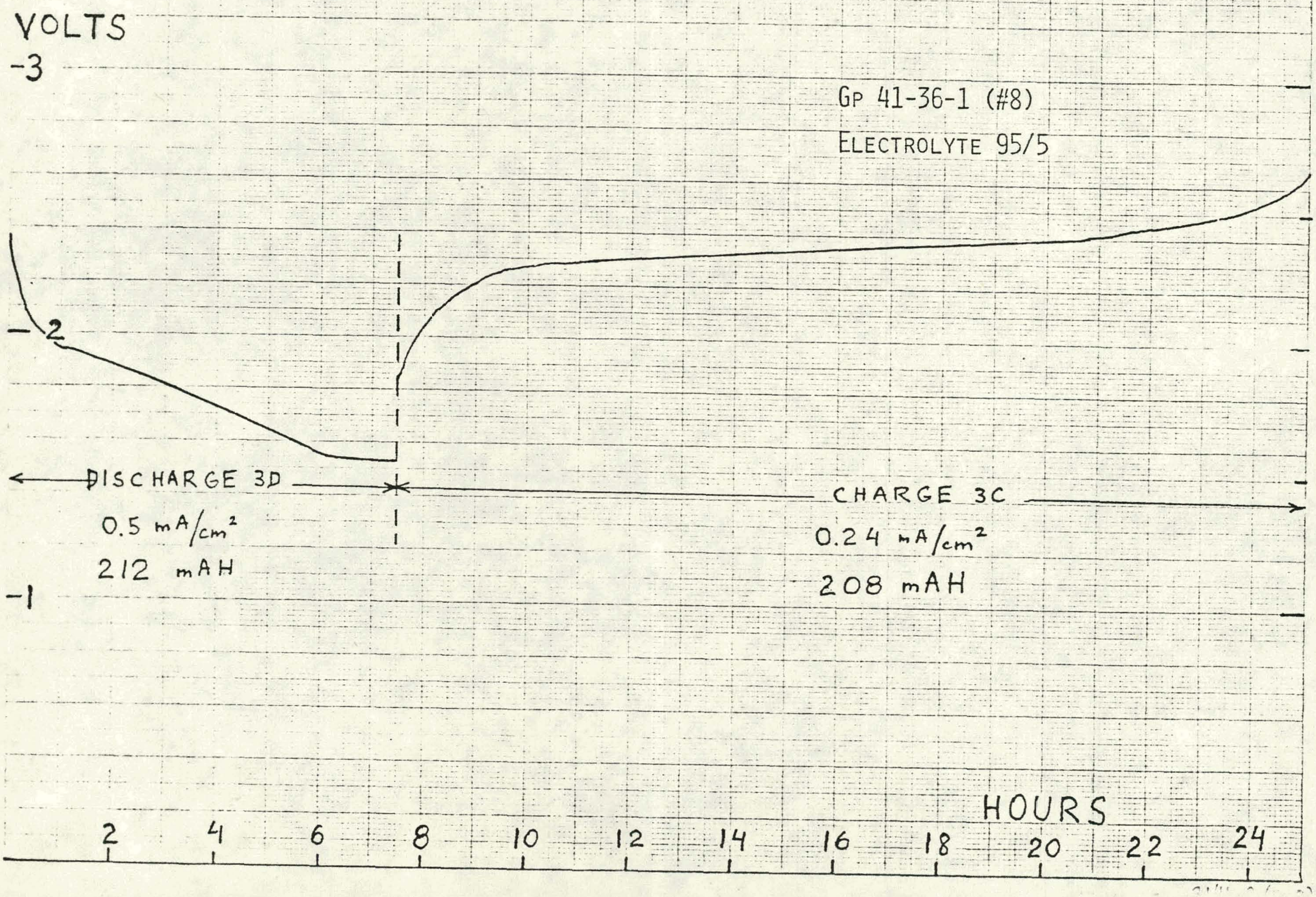
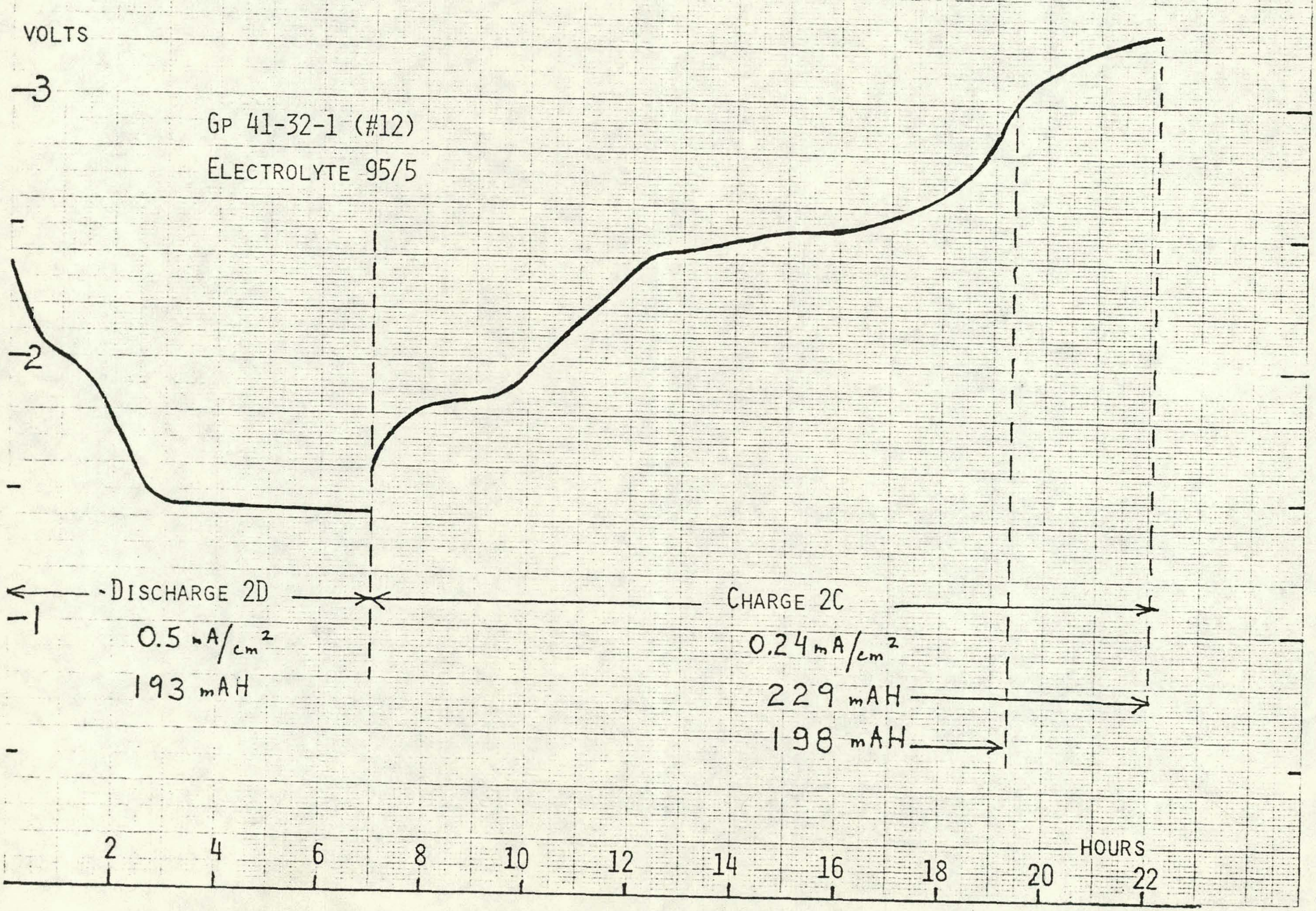


FIG. 2 TYPICAL CYCLE FOR FeS_2-Li CELL



(See Figure 3). These linear graphs over a significant range of cur. densities show the greater polarization for FeS_2 compared to CoS_2. The practical meaning of that is that FeS_2 delivers lower discharge potentials and requires also higher charging potential compared to CoS_2. The state of charge has a very profound effect on the potentials accepted by these cathods. Figures4 illustrates the affect of the state of charge on the cathodic (discharge) potentials of FeS_2 and CoS_2 cathodes. A discharge of only 60 mAH/g lowered the potential of CoS_2 cathodes (vs. lithium electrodes) by approximately 0.4 volts) at 1. mA/cm^2 compared with almost a 1.8 volt drop for FeS_2. The stable slope of the polarization line for the FeS_2 cathode can be readily explained by the larger specific resistivity of this pyrite. However, the large drop between the charged and discharged state is probably due to the formation of compounds much poorer in conductivity than even FeS_2. The simple sulfide CoS is of little further interest in rechargeable ambient temperature lithium batteries since it undergoes reduction to the metallic state and would, therefore, have a limited number of cycle capability. On the other hand, the pyrites can be used reversibly with a discharge of 1 - 1.5 electrons per mole. Of the two, the better conductivity of CoS_2 manifests itself in the form of lower polarization resulting in better charge and discharge potentials compared to FeS_2 in lithium organic electrolyte cells.

4.2.2 Sulfospinel Studies

Two cobalt based sulfospinels have been prepared in our furnaces with a high temperature of 800°C. One is $CoCo_2S_4$ in which cobalt appears in the different ~~and~~ valence states of +2 and +3 state respectively. This material which is designated, as Co_3S_4, occurs in certain materials in nature. The other prepared material is is $CoFe_2S_4$. Complete partial "C" cells were built using these cathode materials with lithium anodes and electrolyte 95/5. A comparison of these was conducted with fully built cells containing CoS and FeS_2 cathodes as illustrated in Table 6. It will be

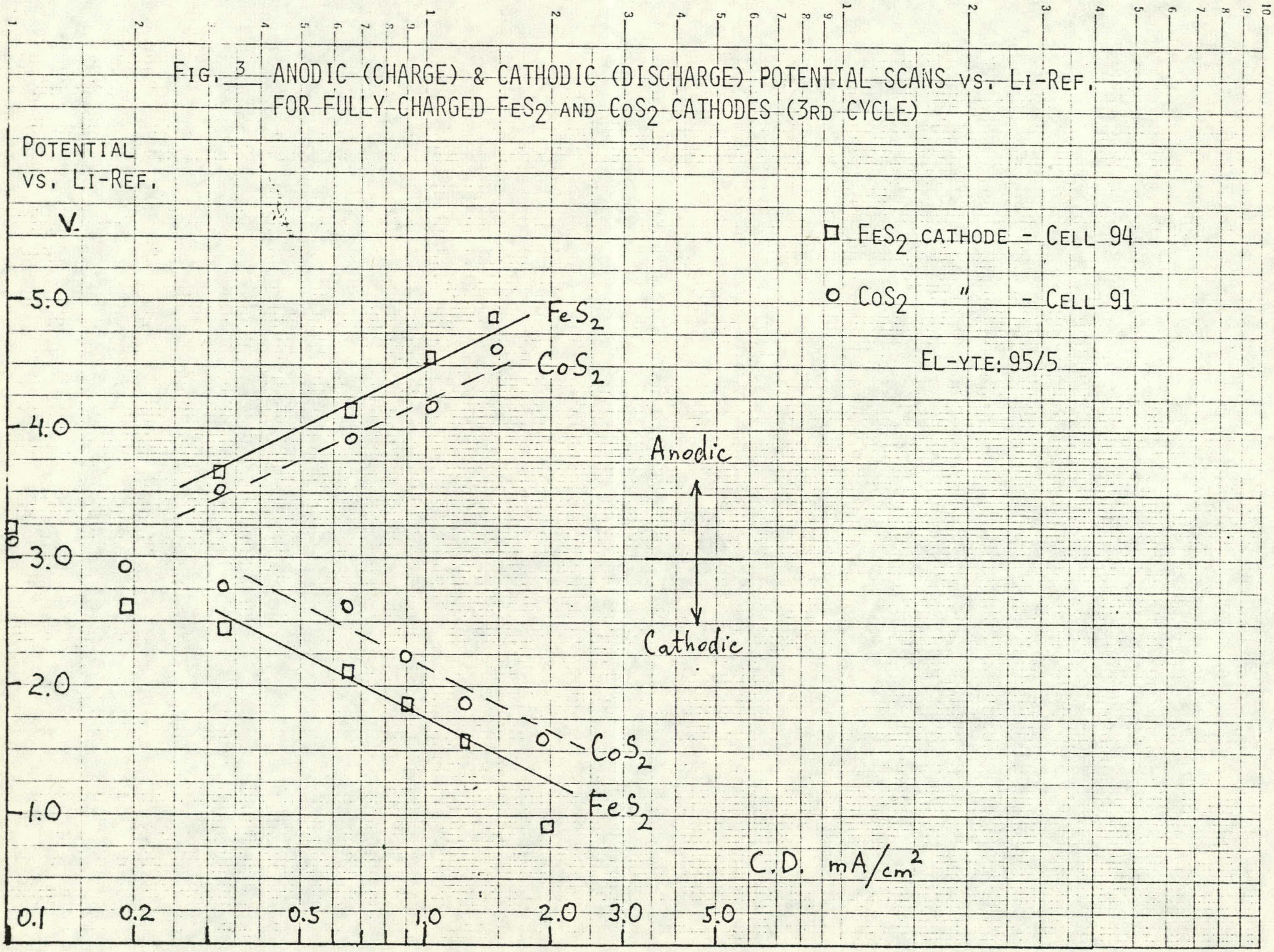


FIG. 3 ANODIC (CHARGE) & CATHODIC (DISCHARGE) POTENTIAL SCANS VS. LI-REF. FOR FULLY CHARGED FeS_2 AND CoS_2 CATHODES (3RD CYCLE)

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3141-4

FIG. 4 EFFECT OF STATE OF CHARGE ON THE CATHODIC (DISCH.) POTENTIAL OF FeS_2 AND CoS_2 CATHODES

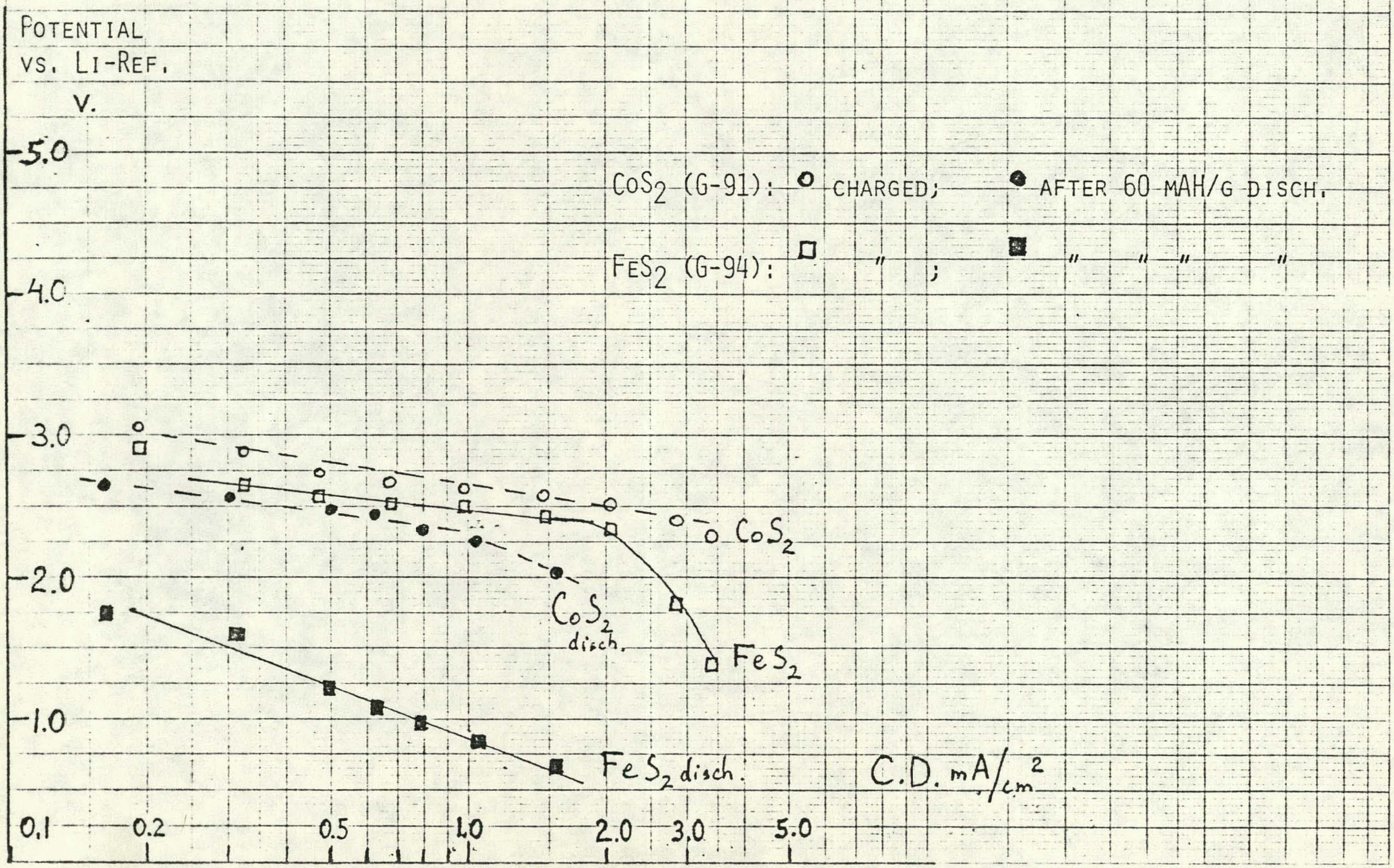


TABLE 6

CHARGE AND DISCHARGE VOLTAGE RANGES FOR FeS_2, CoS, Co_3S_4 AND $CoFe_2S_4$ CATHODES

(El-yte 95/5; Gp. 41/43 - 2,34)

Cycle & Capacity (mAH)	FeS_2	CoS	Co_3S_4	$CoFe_2S_4$
ID: 605 out	2.8 - 1.32	2.54 - 1.25	2.8 - 1.27	2.8 - 1.32
IC: 606 in	1.47- 2.57	1.44 - 3.18	1.43 - 3.17	1.45- 3.31
2D: 500 out	2.2 - 0.85	2.2 - 1.07	2.26- 1.08	2.12- 1.00
2C: 531 in	1.65 - 2.66	1.58 - 2.96	1.53- 2.70	1.60 - 3.20
5D: 526 out	2.38- 1.15	2.35 - 1.18	2.35- 1.13	2.68- 1.06
5C: 528 in	1.85- 2.10	1.77 - 3.51	1.71- 3.52	1.86- 3.80

noted that on the first discharge (1D) of 605 mAH decreasing to approximately 200 mAH/g, all cells had about the same end voltage in the range of 1.25 to 1.32. On charging back the same amount of FeS_2 showed a lower end voltage of 2.58 and the other three groupd of cells showed voltages in the range of 3.17 - 3.31. The differences became more pronounced in the second cycle (2C). This time Co_3S_4 had only an end voltage of 2.70 compared to 3.20 for $CoFe_2S_4$. A higher end voltage of 1.13 (compared to 1.06 for $CoFe_2S_4$) in discharge of cycle 5D may also be significant. From the results of this study, it would appear that Co_3S_4 is more reversible electrochemically than $CoFe_2S_4$. Within the limited scope of the present study phase, there was insufficient time for further comparative evaluation of these two materials.

The third sulfospinel study was that of cobalt and titanium, mainly $CoTi_2S_4$. This material was synthezized in the high temperature furnace from TiS_2, cobalt metal and sulfur through three successive firings through 850°C. X-ray analysis confirmed 95% of the material to have the face-centered cubic structure of the spinel. This cathode material with a 15% addition of graphite and 10% of teflon was evaluated by means of the cathodic and anodic scans in the bell jar glass cell. This study was included with the evaluation of three layered disulfides and for this reason it is discussed in the following Section 4.2.3.

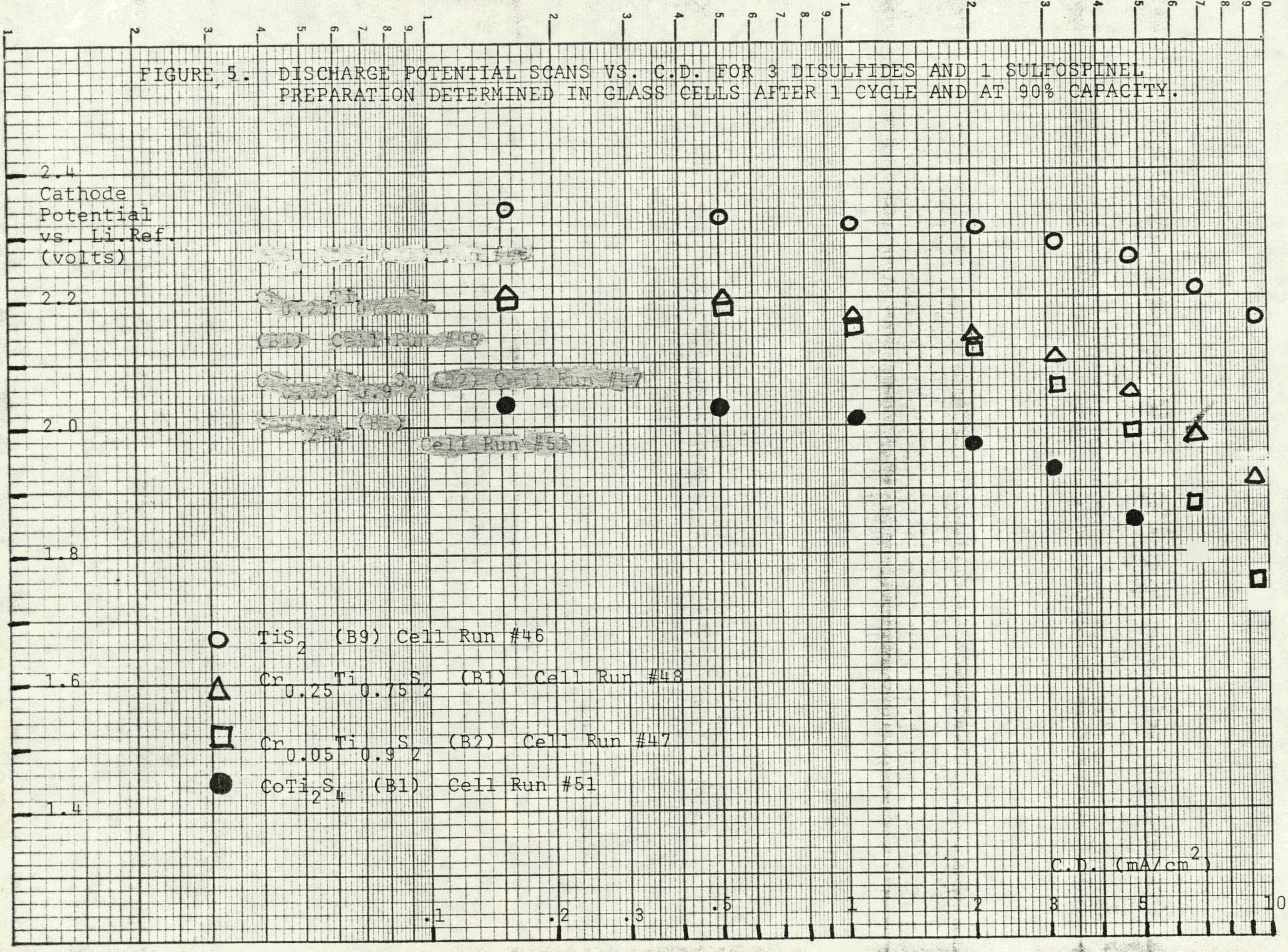
4.2.3 Study of Transition Metal Disulfides

As described earlier, we had initially in the beginning of the program evaluated a commercially available preparation of TiS_2 and TaS_2 and found these materials not to be pure or reproducible. It was the major modification of our design of two-zone quartz furnaces to be able to carry out the synthesis from the elements free of chloride impurities. Since from a point of view of energy density, the heavier tantalum compound is not attractive, we have concentrated on TiS_2 and substituted disulfides of the general formula $M_xTi_{1-x}S_2$.

The reason for our interest in such materials is a indication in the literature (11) that unlike TiS_2 which is a semi-conductor, the substituted compounds exhibit metallic conductivities. On this basis lower effective polarizations of the porous ecectrodes and lower ohmic drops could be anticipated.

In our studies, chromium and molybdenum (Group VIB eliminates) were used for substitutions. The substituted materials were prepared from TiS_2, the matal powders, and a stoichiometric additional amount of sulfur. The mixture was ball milled with an organic vehicle and dried and pelletized to achieve intimate contact during firing at 650 - 750°C. Later we have found it desirable to reduce this temperature closer to 500°. The results for 1 in. x 1 in cathodes prepared with chromium substitutions $x = 0.05$ and 0.25 are illustrated in Figure 5 and 6 in comparison to TiS_2 and the previously mentioned $CoTi_2S_4$. The cathodic potentials (i.e., at discharge) shown in Figure 5 indicate a larger polarization at the high current density of 9.5 mA/cm^2 for the compound with 5 mole % of chromium compared to 25%. In addition the sulfospinel exhibited a [illegible] potential almost 2/10 volts lower throughout the current density range. However, it was capable of sustaining high current densities. It was encouraging that all compounds could discharge at appreciable current densities with reasonably high voltage values. The comparison with TiS_2 may not be of particular interest in Figure 5, because it was from a different batch than the TiS_2 used in the preparation of the two substituted chromium compounds. At these early stages of synthesis, it was not fully realized that slight changes in stoichiometry or final firing temperature may have a pronounced effect on the performance of the disulfide. The charge potentials (anodic) given in Figure 6 indicate a fair parallelism with the cathodic behavior. This means that the sulfospinel $CoTi_2S_4$ which discharges at the lower voltage or charges at the lower voltage than the other compounds promising an extremely good voltage efficiency: for instance, at 3 mA/cm^2

FIGURE 5. DISCHARGE POTENTIAL SCANS VS. C.D. FOR 3 DISULFIDES AND 1 SULFOSPINEL PREPARATION DETERMINED IN GLASS CELLS AFTER 1 CYCLE AND AT 90% CAPACITY.



the charging and discharging voltages would be 2.08 and 1.94 respectively (for a voltage efficiency of 93%).

It is also interesting to note that of the two chromium substituted compounds, again the one with 5 mole % showed a larger polarization than the one with 25%. On the basis of these preliminary results , the $Cr_{o125}Ti_{.75}S_2$ Compound is clearly the better of the two. X-ray analysis for this material confirmed that it has a layered structure similar to TiS_2 with a slight change of the C-axis. The substituted disulfide does operate at higher potentials both on charge and discharge than the sulfospinels, and within reasonable current density limitations, both types of compounds are capable of good voltage efficiencies between charging and discharging.

Partial C-cells were also constructed from these two chromium compounds and from TiS_2 and subjected to cycling. Complete cell voltage charge and discharge scans (not potentials vs. a reference electrode) were made. A sample of the results illustrated for a current density of 3 mA/cm^2 is shown in Table 7. As can be seen on discharge the average voltages of cells containing cathodes made with $Cr_{.25}Ti_{.75}S_2$ were the highest: namely, 1.68 volts compared to only 1.25 volts for the $Cr_{.05}Ti_{.95}S_2$ cathodes. The cells with TiX_2 were in between on charge at the same current density. Again the cells containing $Cr_{.25}Ti_{.75}S_2$ cathodes required the lowest applied potential (which is most desirable) of only 2.2 volts. In this respect the chromium compound with 5 mole % chromium was the poorest requiring 2.6 volts and again TiS_2 was in between in this respect. This trend was observed over a wide range of current densities from .2 to 5 mA/cm^2 on the partial C cells study.

Another series of substituted disulfides involved molybdenum. X-ray analysis was carried out on three molybdenum substituted disulfides of general type $Mo_xTi_{1-x}S_2$. It has been found that for composition x equals <u>0.05</u> the material was a homogeneous disulfide (in agreement with the independent analysis at Argonne). However, for composition x equals <u>0.25</u> and <u>0.50</u> non-homogeneous materials have been obtained (mixtures of TiS_2 and MoS_2). This may be due to the fact that the last two preparations were made using MoS_2 instead of Mo metal. We are planning to investigate this point as well as firing conditions to see if homogeneous disulfide materials can be prepared.

TABLE 7

COMPLETE CELL VOLTAGE SCANS

COMPARISON AT 3 mA/cm^2 (GP. 41-39, 40)

Cathode Material	On Discharge	On Charge
$Cr_{.05}Ti_{.95}S_2$	1.25 v.	2.62 v.
TiS_2	1.50 v.	2.30 v.
$Cr_{:25}Ti_{.75}S_2$	1.68 V.	2.20 v.

Since in the early work the optimum conditions for preparing TiS_2 as a starting material for the substituted compounds were not well established, and the substituted compounds were not always made from the same original TiS_2 batch, some of the conclusions concerning the comparisons must be recognized as tentative and requiring further study.

Mixed layered disulfides involving molybdenum and cobalt at two concentration levels, 5 and 25 mole % have been prepared. These materials were used in the preparation of partial C cells, a study of which is illustrated in Table 8, in comparison to similar cells with TiS_2. As can be seen, the first discharge resulted in very close results for all compounds. However, upon charging back of 212 mAH/g (i.e., 5% excess over the amount removed in the previous discharge). all cells attained high

TABLE 8

COMPARISON OF

MIXED LAYERED DISULFIDES AND TiS_2

(Gp. 41-38, El-yte 95/5)

	$Co_{.05}Ti_{.95}S_2$	$Mo_{.05}Ti_{0.95}S_2$	$Mo_{0.25}Ti_{0.75}S_2$	TiS_2	$Co_{0.25}Ti_{0.75}S_2$
End-V. after 1st disch. of 202 mAH/g	1.18 v.	1.12 v.	1.08 v.	1.11 v.	1.15 v.
End-V. after 1st charge of 212 mAH/g	3.73 v.	3.40 v.	2.69 v.	2.6-3.5v.	3.5 v.
5th cycle cap. out to 1.3 v mAH	300	100	130(est)	300	~90
5th cycle End-V. after charge of 100 mAH/g	2.3-2.9 v.	3.8 v.	3.9 v.	2.4-3.8v	2.5 v.

voltages except for $MO_{.25}Ti_{.75}S_2$ and some of the titanium disulfides. In the fifth cycle the capacity output, however, was best for TiS_2 and the cobalt substituted $Co_{.05}TiS_{.95}S_2$. These two types of cells were also exhibiting lower charging voltages in the subsequent charging step. X-ray analysis indicated that the 5% Co substituted compound had a TiS_2 structure and so did the 2 molybdenum substituted materials. However, the cobalt material at 25 mole % had predominently a structure of the spinel $CoTi_2S_4$. In the original preparation of this material the second firing employed a temperature of 800°C which later was found to be destructive of TiS_2 structures. It is therefore not clear at this point whether the tendency to form the spinel rather than retain the layered TiS_2 structure is due to the high temperature or other attempted stoichiometry. Apparently this was not a problem at the 5 mole % level and, therefore, the question regarding cobalt substitutions still remains open.

A vanadium substituted titanium disulfide was prepared from TiS_2, vanadium metal powder and a required amount of sulfur with a formal composition $V_{.25}Ti_{.75}S_2$. This material is known to exhibit metallic conductivity (11). It was therefore interesting to compare the two under similar conditions of cell structure. Table 9 illustrates results for two groups of TiS_2 cells employing electrolyte 95/5 and electrolyte 43/6 (similar to 95/5 except containing 30% DME instead of 25%). The vanadium substituted material was studied only in electrolyte 95/5. Referring at this time to the results in electrolyte 95/5, it can be seen that the vanadium compound, after 17 cycles showed slightly higher cell voltages which became more significant with increasing current density on scanning. The differences became more significant, however, after a partial discharge of the cells as shown in Table 9 after discharge of 100 mAH/g. The vanadium substituted material cells gave significantly larger cell voltages (1.80 - 1.86 v. vs. 1.40 - 1.62 v.), at the end of the first cycle. Higher voltages were also demonstrated after the 17th cycle. Furthermore, during charging the vanadium material

TABLE 9

Comparison of TiS_2 & $V_{0.25}Ti_{0.75}S_2$

Discharge Voltage Scans for Charged Cells (Gp. 17 - 14)

	TiS_2 (B-30)				$V_{0.25}Ti_{0.75}S_2$	
	Gp. 1 El. 95/5		Gp. 6 El. 43/6		Gp. 2 El. 95/5	
C.D. mA/cm^2	Cycle 1	Cycle 17	Cycle 1	Cycle 17	Cycle 1	Cycle 17
0.25	2.30 v.	2.34 v.	2.65 v.	2.61 v	2.29 v.	2.35 v.
0.50	2.23 v.	2.26 v.	2.55 v.	2.50 v	2.20 v.	2.30 v.
0.75	2.18 v.	2.20 v.	2.49 v.	2.36 v	2.15 v.	2.24 v.
1.25	2.08 v.	2.08 v.	2.41 v.	2.10 v	2.04 v.	2.14 v.
Cell Voltages after disch. of 100 mAH/g - in Cycle 1	1.40 - 1.62		0.80 - 0.91		1.80 - 1.86	
- in Cycle 17	1.60 - 1.71		1.49 - 1.70		1.75 - 1.79	

exhibited cell EMF's 0.1 - 0.15 v. lower than the straight TiS_2.

The results of this section of the studies indicate that layered disulfides are very promising for ambient temperature lithium cells. The preparation of TiS_2 requires careful attention to the problem of impurities, stoichiometric ratios, particle size and the firing temperatures. The substitution of vanadium, chromium and possibly molybdenum offered the possibility of improving conductivity of the material and, therefore, lowering its effective polarization during cell charge or discharge.

4.2.4 N-Butyl Lithium Titrations of Cathode Materials

It is desirable in the search for new cathode materials for ambient temperature Lithium batteries to have a rapid survey method to determine electrochemical activity. Lithium organometallic compounds dissolved in a non polar solvent such as Hexane can reduce chemically cathodic materials and/or appropriately intercalate Li into them. One recently suggested compound is N-Butyl Lithium (C_4H_9Li) (12). For instance, in case of TiS_2 the following reaction takes place:

$$C_4H_9Li + TiS_2 \longrightarrow Li\,TiS_2 + 1/2\ C_8H_{18}$$

After treating the compound to be determined with an excess of wolution the exact amount of equivalents is determined by a back titration with acid. It should be noted that this valuable non-electrochemical test gives only the extent to which the cathodic material can be reduced and does not necessarily indicate intercalation, i.e. any potential crystallographic reversibility.

Early in this program a number of compounds have been titrated with N-Butyl Lithium as shown in Table 10. The first two entries show two commercial grades of TiS_2. The theoretical result for TiS_2 should be 1.0 Equiv/mole (240 mAH/g). The deviation of the results for these commercial materials from unity and from each other confirm the discrepancies and difficulties with these materials experienced in cell studies due

TABLE10 - RESULTS OF N-BU-LITHIUM TITRATIONS OF SELECTED CATHODE MATERIALS

Mat. Code	Formula	Source or Batch #	Preparation	Equiv/mole	mAH/g
TiS_2	TiS_2	Cerac		1.36± 9%	325
TiS_2	TiS_2	Gt.Wstn.		.91± 15%	217
TaS_2	TaS_2	Cerac		.79± 1%	86
TS-4	$CuS \cdot TiS_2$	Gt.Wstn.		2.15± 1%	278
TS-6	$CuFe_2S_4$	Cop.	Vac dried unfired	5.55± 5%	490
TS-10	$CuCo_2S_5$	Cop.	Vac. dried	7.46	585
TS-11	$CoFe_2S_4$	Cop.	Vac. dried	6.15± 4%	551
TS-11(B4)	$CoFe_2S_4$	B4	From elem. F. in evac. quartz comp.	5.35	480
TS-12	$CoS.TiS_2$	Gt.Wstn.		1.25± 3%	165
CuS	CuS	Cerac		1.24	348
Chalcopyrite	$CuFe\ S_2$	Wards	Vac. dried	1.51± 9%	221
$Fe\ S_2$	$Fe\ S_2$	Argonne		2.4	536

to impurities. The next layered disulfide TaS_2 showed a low equivalent number.

The complex sulfides developed by Electrochimica Corporation (TS-compositions) all show high equivalent values. It should be noted that TS-4 and TS-12 are not sulfospinels but 1:1 solid solutions. There is a considerable difference between these two compounds. Compositions TS-6, -10 and -11 show very high values of the order of 5 - 7 equiv/mole. For TS-11 the determination was made with the material as coprecipitated and vacuum treated and the fully fired material. The slight change from <u>6.15</u> to <u>5.35</u> equiv/mole is probably due to the elimination of volatile reducible materials.

The last column giving the capacity parameter per unit weight of the cathode material (mAH/g) is of engineering interest. Accordingly the sulfospinels TS-4, -6, -10 and -11 are all very attractive on a weight consideration basis.

4.2.5 <u>Results in High Temperature Cells</u>

During this program several samples of cathode materials have been forwarded to the Chemical Engineering Division of our Argonne National Laboratory for evaluation in high temperature molten salt (KCl - LiC) cells at 420 - 450°C. The anode in such cells is a lithium aluminum alloy which puts little practical limitations on current densities both on charge and discharge. Furthermore the cycling ability in high temperature cells is not limited by the electro- crystallization of the lithium in the way it is experienced in organic electrolytes, therefore a better evaluation of the cathodes is unhindered by the limitations of the anode. The results of a recent series of tests conducted at the current densities 13 - 39 mAH/cm^2 at Argonne are illustrated in Table 11 in which the Faradeic capacity per gram is studied for all the compounds on the basis of 1/2 mole lithium per [illegible]
The Faradaic utilization efficiency 1.0 S column thus relates the actual capacity obtained to that based on the weight of the active material in the cell and in its Faradeic capacity. The

TABLE 11

HIGH TEMPERATURE CELL PERFORMANCE OF ELECTROCHIMICA CATHODE MATERIALS AT 420-450°C

Material	Batch#	Cell#	Performance Rating	Theo. Cap. AH/g *	C.D. mA/cm^2	Farad. Util. Efficiency % of Theo.	Typical C.E.%
$Cr_{0.25}Ti_{0.75}S_2$	B-1	AJ-1B	Good	0.237	26	$\frac{.296AH}{.498AH} = 60\%$	93-97%
$Cr_{0.05}Ti_{0.95}S_2$	B-2	AJ-2	Fair	0.239	13	$\frac{.216}{.478} = 45\%$	80%
$CuTi_2S_4$	TSB-B1	AJ-3	Very Good	0.186	26	$\frac{.360}{.410} = 88\%$	93-100%
$Mo_{0.05}Ti_{0.9}S_2$	B-2	AJ-4	Very Good	0.239	13 39	$\frac{.300}{.479} =$ 80% 64%	94-98% 98-100%
TiS_2	B-18	AJ-5	Fair	0.239	26	$\frac{.280}{.479} = 58\%$	93-97%
$Mo_{0.25}Ti_{0.75}S_2$	B-2	AJ-6	Poor	0.217		= 17%	43%

*) For 1/2 mole Li per 1 S

current efficiency column related to capacity obtained during discharge vs. capacity charged in.

As can be seen the TiS_2 compound (batch B 18) was only a fair material since its Faradaic utilization efficiency was only 58%. However, some of the substituted layered disulfides made from this compound were superior to it. It is extremely important that comparisons of this type be made with the TiS_2 from the <u>batch</u> from which substituted compounds were synthesized. The following conclusions can be made on the basis of the results of Table 11.

1. Compound with $Mo_{0.25}$ was comparatively poor.
2. Compound with $Cr_{0.05}$ was only satisfactory.
3. However, all other compounds showed superior utilization compared with TiS_2 namely 50% for $Cr_{0.25}$, 64 to 80% for $Mo_{0.05}$ and 88% for the copper spinel all compared to 58% for the TiS_2 <u>from which these compounds were made</u>.
4. The performance of the $Mo_{0.05}$ substituted disulfide is particularly impressive also on the basis of an excellent current efficiency of 98 to 100% even at a current density of 39 mA/cm^2.
5. The sulfospinels $CuTi_2S_4$ emerged as one of the best in this group of compounds studied in the high temperature cells. It was capable of operating at the high current density of 26 mA/cm^2 with an 88% Faradaic utilization efficiency and a current efficiency of 93 - 100%. This performance was far superior than in organic electrolyte cells.

Because of the removal of the limitations of anode performance and a superior cathode kinetics in the high temperature cells, it would appear that some materials which only showed a fair performance in the room temperature cells, such as the spinel $CuTi_2S_4$ or the $Mo_{.05}Ti_{.9}S_2$ disulfide could deliver very superior performances in high temperature. This may provide an important hint for the direction future investigations of these compounds ought to be. It is also interesting to note regarding the two chromium substituted disulfides that the 25 mole % chromium compound was clearly superior to the 5 mole % material, and what is most important, it was superior to the TiS_2 from which it was made.

4.2.6 Preliminary Evaluation of Electrolyte Composition

During this program it became clear that electrolyte has a profound effect on performance of sulfide cathode materials. Lithium perchlorate solutions in THF - DME mixtures (as typically in electrolyte 95/9) were then adopted for most of the evaluation studies of the sulfide materials as cathodes. Perchlorate-ether mixtures, however, are generally not considered safe mixtures. It was, thus, desirable to seek substitutions. An additional preliminary electrolyte study was, therefore, added towards the end of the program.

As alternatives to the lithium perchlorate, $LiAlCl_4$ and $LiAsF_6$ were studied. In the area of solvents, propylene carbonate (PC), methyl acetate (mA), and sulfur dioxide were considered. Tests of this type have been carried out--a sample of which is given in Table 12 in which 4 electrolytes are compared in respect to the end voltage as a certain discharge and subsequent recharge. As can be seen, the standard electrolyte 95/5 gave the highest end voltage on discharge and the lowest upon recharge (1.9 - 2.6 v. respectively), i.e., the most desirable characteristics. The next best electrolyte in this respect was 14 B/6, although it required an additional volt towards the end of the charge. The addition of SO_2 to the methyl acetate, in accordance with a recent Electrochimica Corporation patent (13, 14) appears definitely helpful, but it does not overcome the disadvantage of using the AsF_6^- anion for the same solvent system. By comparing electrolyte 16/6 to 95/5 it is very clear, however, that AsF_6^- is inferior to ClO_4^-. The following conclusions have been arrived at in these preliminary electrolyte studies:

TABLE 12

EFFECT OF ELECTROLYTE ON TiS_2 CAPACITIES AND CHARGING VOLTAGES (GP. 41-39-1 to 6)

El-yte No.	14A/6	14B/6	16/6	95/5
Composition	1.8 m/L $LiAsF_6$ 100 MA	1.8m/L $LiAsF_6$ 1.0 SO_2 100 MA	1.8m/L $LiAsF_6$ 75 THF 25 DME	2.5 m/L $LiClO_4$ 75 THF 25 DME
(3D) End V. after dis. 130 mAH/g	0.9-1.4 v.	1.8-1.9 v.	1.45 v.	1.90 v.
(2C) End V. after charge	4.10 v.	3.6 v.	4.6 v.	2.6 v.

a) Propylene carbonate is an extremely poor solvent for these compounds even with perchlorate anion

b) $LiAlCl_4O_4$ is totally unacceptable for rechargeable cells.

c) $LiAsF_6$ is poor and tends ~~to turn to~~ towards high charging voltages.

d) There may be some possibilities for the use of MA, particularly with additions of SO_2 and perhaps a greater safety with PC's, but this area remains to be thoroughly investigated.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The basic objective of this work was the study of two new classes of cathode materials of potential value for ambient and high temperature high energy rechargeable batteries employing lithium anodes. The compounds of interest are sulfospinels and layered disulfides of transition groups IVb and Vb. Mid point in the program, the evaluation of the simple sulfide COS and of the 2 pyrites COS_2 and FES_2 was added.

The basic tasks were the synthesis of these materials and their preliminary electrochemical evaluation. In addition, it was necessary to develop and evaluate some electrolyte formulations to enable carrying out the neccssary electrochemical studies on these compounds.

Three synthetic methods were studied:

A. Coprecipitation of sulfides followed by some form of a high temperature reaction.

B. Preparation from elements by vapor phase reaction.

C. Synthesis from simpler sulfides by high temperature reaction.

Second method became the major synthetic tool during the second half of the program.

In the area of synthesis, the following guidelines were learned:

A. TiS_2 is best synthesized in the temperature of 500 - 600°C with 2 - 3 firings.

B. Layered disulfides are best obtained by starting with a good grade of TiS_2 and operating in the same temperature range. 2 firings are usually sufficient.

C. Sulfospinels are best prepared in the range of 650 - 850°C with a 200 - 400 differential to the sulfur temperature zone.

D. For mixed compounds of both types, intimate contact achieved in pelletizing is very important.

Early in the program it was established that lithium perchlorate electrolytes in the ether mixture of tetrahydrofuran-and dimethoxy ethane are the best vehicles for evaluation of the sulfide cathode materials. Subsequent efforts during the program to substitute the ClO_4^- anion by AsF_6^- or $AlCl_4^-$ led to very irreversible cells or to outright failures. Some possibilities of using MA mixtures with SO_2 were found, but this was not fully explored because of time limitations (see Section 4.2.6). For most of the cathode studies $LiClO_4$ solutions in THF - DME were employed.

From the study of the simple transition metal sulfides COS, COS_2, and FeS_2 (Section 4.2.1), the following conclusions can be drawn:

A. All materials can be used for cathodes although their cycling capability remains to be extablished.

B. COS delivered approximately 1 and COS_2, 1.33 electrons per mole to a 1.1 v. cutoff. The latter also charges to a lower end voltage than the simple sulfide which is understandable since the pyrite is a better conductor.

C. FeS_2 to the same cutoff voltage yields 230 mAH/g or 1.02 electrons per mole.

D. Most of the discharge of these simple sulfides occurs in the range of 1.5 to 1.0 v. cCharging is easily completed at 2.2 volts; hence, voltage efficiency is very high.

E. Because of the better conductivity of COS_2, it is superior to FeS_2 in lithium organic electrolyte cells in respect to charge and discharge polarization.

In the area of sulfospinels, (Section 4.2.2) CO_2S_4 (= CO_3S_4) and $COFe_2S_4$ were studied. These materials were capable of considerable capacity densities as to 605 mAH/g. However, further action of reversible cycling was deliberately limited to 200 mAH/g. Within the limited study carried out, CO_3S_4 appeared more reversible electrochemically than $COFe_2S_4$. A third sulfospinel prepared was $COTi_2S_4$ for which a very clear x-ray pattern of 95% of a face-centered cubic structure was obtained. This material was capable of high current densities up to 10 mA/cm^2 in polarization scan. It's charging and discharging voltage ranges are similar to those of the other 2 sulfospinels. It indicates an extremely good voltage efficiency, e.g., of 93% at 3 mA/cm^2.

The study of the transition metal disulfides covered mainly TiS_2 and the substituted $M_xTi_{1-x}S_2$ (Section 4.2.3). Once the proper conditions for synthesis were established, and good quality materials could be prepared, some trends emerged.

The following conclusions can be drawn from this section of the work:

A. The preparation technique for the disulfides and their stoichiometric ratios are very critical for the electrical performance.

B. Properly prepared TiS_2 and substituted $M_xTi_{1-x}S_2$ compounds operate very reversibly through intercalation of lithium ions on discharge and their release upon charge.

C. The chromium compound, the one with 25 mole %, was far superior to the one with 5 mole % and also to TiS_2, from which it was originally prepared, both in terms of higher output voltages on discharge and lower required voltages.

D. For molybdenum substituted compounds of the type $Mo_xTi_{1-x}S_2$, on the other hand, the 5 mole % material was the only homogeneous one obtained. Attempts to prepare the 25 and 50 mole % resulted in mixtures of TiS_2 and MoS_2 according to x-ray analysis.

E. An attempt to prepare the $Co_{.25}Ti_{.75}S_2$ resulted in a predominently sulfospinel structure of $CoTi_2S_4$, and consequently, electrochemical behavior was similar to that of the latter.

F. The vanadium compound $V_{.25}Ti_{.75}S_2$, which is known to exhibit metallic conductivity (11), gave in initial limited study, significantly larger discharge voltages than TiS_2 and required up to 150 mA more charging voltages.

From the studies so far performed, it emerges that the 25 mole % vanadium and chromium substituted disulfides are superior to TiS_2. The N-Butyl lithium titration technique was found valuable as a screening method for potentially valuable cathode materials. It's one disadvantage is, of course, that it cannot distinguish between intercalation and compound reduction.

Results in high temperature cells (Section 4.2.5) of the material submitted by Electrochimica Corporation to Argonne National Laboratory were most encouraging and generally paralleling the findings in the lithium organic cells. Of course, in the high temperature cells, much higher current densities could be demonstrated than in the ambient temperature cells. Indeed, the range employed was 13 - 39 mA/cm^2. The following conclusions can be reached from this work (See Table 11):

A. The substituted compounds S_2, $Mo_{.05}Ti_{.95}S_2$, and $Cr_{.25}Ti_{.75}S_4$ were superior to the TiS_2 from which they were made in Faradaic utilization efficiency and in current efficiency.

B. A sulfospinel $CuTi_2S_4$ emerged as one of the best materials capable at 26 mA/cm^2 of an 88% utilization efficiency and a current e efficiency up to 100%. Compounds with nominal composition $Cr_{.05}$ and with $Mo_{.25}$ were either fair or poor in parallel findings in the ambient temperature organic cells.

It also appears that the tests of high temperature cells are not limited by the cycling ability of the lithium anode and, therefore, there are lesser limitations on the cell evaluation through cycling. The high temperature cell tests were, therefore, an important corroboration in establishing the value of substituted TiS_2 as a potentially important future cathode material.

In summary, the work of the past year has resulted in the determination of several compounds of the sulfospinel type and of the layered disulfide type which are promising for rechargeable ambient temperatire organic electrolyte battery systems and as well as for high temperature molten salt lithium anode batteries.

Future work in this area should go in several directions:

A. A crystalographic study of the structure of the new substituted disulfides which have given initial promising results in order to evolve guidelines for directing future synthetic efforts and for understanding of the reaction mechanism.

B. Further investigation of optimum methods for preparing of desirable compounds.

C. Development of a mechanically desirable and reproducible cathode structure as a necessary base for comparison of cathodic materials in respect to polarization on charge and discharge and of efficiency as cycling proceeds.

D. Development of a reliably sealed cell design to undertake cell parameter performance studies in a systematic manner.

E. Further development work on the organic electrolytes from the point of view of the following considerations:

1. Safety.
2. Non-participation on the cathodic and anodic process at both electrodes.
3. Chemical stability towards electrode materials and goods.
4. Providing a good basis for lithium anode rechargeability or electro-crystalization.

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