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# ONR LONDON CONFERENCE REPORT

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INTERNATIONAL MEETING ON LITHIUM BATTERIES
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## INTERNATIONAL MEETING ON LITHIUM BATTERIES

An international meeting on the topic of lithium batteries was held in Rome from 27 through 29 April 1982. The papers highlighted research results in the electrochemistry of lithium batteries. Relatively little emphasis was placed on actual battery systems; in many respects, this made the meeting of general value. Applied lithium battery work has been reported at international meetings such as the power sources conferences in Brighton and Atlantic City.

The Rome meeting was organized by Dr. S.B. Brummer (EIC Laboratories, Inc., US), chairman, and Dr. B. Scrosati (Univ. of Rome), secretary, and was sponsored by the Italian Chemical Society and the Electrochemical Society (US). The meeting was attended by about 120 participants representing 19 countries. The scope of representation attests to the present interest in lithium as an active battery component. Essentially all the participants had some direct involvement with such systems.

Sessions of the conference addressed the following aspects of lithium battery technology: lithium cyclability, lithium passivation, oxide cathodes, insertion cathodes, solid electrolytes, and polymer electrolytes. In addition, there was a general session on safety and two specific battery systems.

### Lithium Cyclability

Brummer opened the conference and the session on lithium cyclability with a review of the problems associated with lithium recyclability and a summary of the progress (much of it by EIC) in solving the problems. It is well established that the recharging of lithium is impeding the development of lithium secondary batteries. While lithium can be plated with almost total efficiency, subsequent stripping of the deposits is inefficient. The efficiency of discharge tends to deteriorate on cycling. Lithium deposits are often

dendritic; this complicates the design of long cycle life batteries. Finally, passivation of the deposits can occur on stand. Brummer discussed strategies that have been explored to improve the efficiency of lithium cycling, including the use of alloys, surface-active additives, scavengers, and solvent and electrolyte purification schemes. He thinks that the solvent/electrolyte properties and purification are the most promising variables for improving cycling efficiency.

This is the approach EIC has been using with considerable success. For example, EIC has fabricated and tested prismatic cells in two sizes, 5 to 6 ampere-hours (Ah) and 20 Ah. The former deliver 2.1 V when cycled at the approximately C/20 rate continually for 50 to 100 times. The 20 Ah cells have a voltage of 1.9 and cycle over 50 times at C/20. Based on EIC's experience, Brummer made the following points about experimentation on lithium cycling: the use of non-lithium substrates produces invalid results; electrolyte volume and composition have to correlate with "real world" conditions. In general, valid cycle data are achieved in scaled cells having battery geometries and cycled under realistic conditions of rate and depth of discharge. He closed his presentation by identifying issues that still need to be addressed, such as low temperature performance, adequate separator materials, and the broad subject of surface films' formation, stability, and effects on the cycling process. The subject of surface films is one of the more complex associated with lithium electrochemistry, and other speakers addressed the topic.

Dr. Robert Somoano (Jet Propulsion Laboratory [JPL], US) reported results from his group's studies of the electrochemistry of the EIC system: lithium-titanium disulfide ( $\text{Li-TiS}_2$ ) cells using a 2-methyltetrahydrofuran/lithium hexafluoroarsenate electrolyte. Somoano measured the oxidative stability of the  $\text{TiS}_2$  cathode material and found it to be stable in the system. ESCA studies

of the electrode surfaces after exposure to the electrolyte have provided some insight into the nature of the films. Lithium arsenic oxyfluorides have been observed at the lithium surfaces, and a  $\text{TiO}_2$  layer is present on the  $\text{TiS}_2$ .

The presence of alkoxides among the reaction products was reported. The JPL group is proposing the use of sulfolane, or substituted sulfolane (e.g., 3-methylsulfolane), or both as a solvent for secondary lithium systems. The group has made another contribution to secondary lithium battery development in their work on the use of ethylene-propylene diene terpolymer as an elastomeric binder for  $\text{TiS}_2$ . The resulting cathodes are flexible and cycle well.

In related papers on lithium cyclability, M. Garreau (Univ. Pierre et Marie Curie, France) described an investigation of lithium-aluminum alloy electrodes, which, as mentioned above, offer one possible solution to the lithium reactivity problem. K.M. Abraham (EIC Laboratories) described the use of solvent blends containing tetrahydrofuran to increase electrolyte conductivity; V.R. Koch (Covalent Associates, US) discussed the factors influencing the reactivity of organic electrolytes with lithium. Garreau measured average corrosion current densities for Li-Al alloy in propylene carbonate and dioxolane-based electrolytes. He also reported a value for the chemical diffusion,  $D$ , of lithium into LiAl of about  $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ . Cycling efficiencies near 90% were obtained with LiAl electrodes. Abraham and Goldman showed that blended solvents can be used to effect desirable electrolyte characteristics. For example, tetrahydrofuran/2-methyltetrahydrofuran mixtures exhibit, with only small degradations in cycling efficiency, higher conductivities and lower freezing points than 2-methyltetrahydrofuran-based electrolytes. Koch discussed the role of impurities, the supporting electrolyte anion, and solvent molecular electronic and structural properties in

the reactivity of the electrolyte with lithium. He also pointed out the need to understand the nature and control of interfacial films.

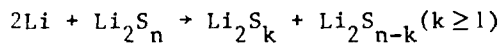
#### Lithium Passivation

Several papers dealt specifically with surface films and lithium passivation. E. Peled (Tel-Aviv Univ., Israel) reviewed his solid electrolyte interphase (SEI) model and presented data on the SEIs in various systems. The proposed SEI is a surface layer about 2-nm thick, formed immediately by the reaction of the electrode with the electrolyte. The layer behaves as a solid electrolyte. For the alkali and alkaline earth metals in thionyl chloride, the layer is the respective chloride, which has a resistivity of  $10^7$  to  $10^8 \Omega\text{-cm}$ . Lithium in the presence of propylene carbonate forms lithium carbonate ( $0.5$  to  $2.5 \times 10^8 \Omega\text{-cm}$ ), and in the lithium/THF-lithium polysulfide system, the SEI is lithium sulfide ( $\text{Li}_2\text{S}$ ) ( $1$  to  $4 \times 10^7 \Omega\text{-cm}$ ). The overall passive layer proposed consists of the SEI at the metal-film interface and a thicker porous layer at the SEI-solution interface.

Y. Geronov (Bulgarian Academy of Sciences) and B. Scrosati (Univ. of Rome) in separate papers presented evidence for a two-layer passivation film. Geronov investigated films formed in the lithium-sulfur dioxide system (containing acetonitrile) for various supporting electrolyte salts. At low sulfur dioxide concentrations (12% by weight), the corrosion rate is rapid. The presence of water increases the rate of film growth. Bromide, perchlorate, and tetrachloroaluminate exhibit nearly the same film growth rate. Hexafluoroarsenate behaves differently; the porous layer does not appear to form and the rate of corrosion is low. Scrosati's results were obtained for the lithium-sulfuryl chloride system using complex plane impedance techniques.

H. Yamin and E. Peled (Tel-Aviv

Univ.) described the lithium-sulfur battery they developed recently. The battery has received considerable publicity in the trade journals because of its potentially very high energy density. Button cells of 275 and 500 milliampere-hour (mAh) capacities have been made and tested. Based on the cell components without the case, the cells have energy densities of 730 and 1,130 wh (watt-hours)  $\text{kg}^{-1}$ , respectively. The cell chemistry is given by the general equation:



To overcome the problems of corrosion but retain sufficient electrolyte conductivity, Yamin and Peled used an electrolyte containing lithium polysulfide and lithium perchlorate in tetrahydrofuran-toluene mixtures. The toluene apparently surpresses the lithium sulfide solubility, thereby stabilizing the passivating film at the lithium anode. Consequently, the cells have shown good storage behavior and stability at 60°C. The cells are low rate; discharge current densities to 40 microamperes per square centimeter ( $\mu\text{Acm}^{-2}$ ) were reported.

M. Babai (Tadiran, Inc., Israel) reported on lithium-thionyl chloride cells of 8- to 11-Ah capacity for high temperature applications. Cells have been discharged at temperatures to 150°C. The usable capacity was highest at the higher discharge rates (less than 2 months of discharge). The self discharge rate remains low at 150°C. The open circuit voltage of the cells increases continuously on storage at 120 and 150°C, while it remains constant at 72°C.

Mr. C. Dhamelincourt et al. (Centre Nationale de la Recherche Scientifique [CNRS], France) have obtained Raman spectra for lithium tetrachloroaluminate in sulfur dioxide, thionyl chloride, and mixtures of the two. They propose the formation of a mixed solvate of the type

$\text{Li}_n\text{SO}_2 \cdot m\text{SOCl}_2$ ; the best fit was obtained when  $n=m=1$ .

#### Oxide Cathodes

G. Pistoia, (Consiglio Nazionale delle Ricerche [CNR], Rome) opened the session on oxide cathodes by reviewing the mechanistic aspects of reversible oxide electrode materials. He described the various structural types of oxides, such as the layered compounds molybdenum trioxide ( $\text{MoO}_3$ ) and lithiated cobalt dioxide ( $\text{Li}_x\text{CoO}_2$ ); the framework transition metal oxides based on interconnected  $\text{MO}_6$  octahedra, e.g., titanium dioxide ( $\text{TiO}_2$ ); and rhenium trioxide ( $\text{ReO}_3$ )-related structures, particularly the vanadium oxide with stoichiometry  $\text{V}_6\text{O}_{13}$ , hexagonal tungsten trioxide ( $\text{WO}_3$ ) structures, and manganese dioxide ( $\text{MnO}_2$ ). He discussed work on the use of oxides of these structures as cathodes and the effects of ion insertion on the structure of the materials. The rutile structures are not yet useful for electrodes.  $\text{ReO}_3$  has a flexible structure that can twist on lithium ion insertion. External edge sharing, such as is found in  $\text{V}_6\text{O}_{13}$ , gives a more rigid framework with better reversible intercalation behavior. The requirements for fast diffusion are sufficiently large bottlenecks within the lattice sites and a reduced tendency toward covalent lithium-oxygen bonds. Many of the oxides have potentially high gravimetric energy densities, e.g.,  $\text{Li}_x\text{CoO}_2$ , 1,100 wh  $\text{kg}^{-1}$  at 0.92 $\text{Li}^+/\text{Co}$  and  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ , 670 wh  $\text{kg}^{-1}$  at 1  $\text{Li}^+/\text{V}$ .

K. Hampartzumian et al. (Bulgarian Academy of Sciences) discussed the design and development of a multicell lithium-manganese dioxide 9-V battery to replace the LeClanche battery and the Krona VC, a zinc-air battery produced in

the USSR. A layer stack design proved to be superior in polarization and capacity to both the LeClanche and Krona VC. The anode (Li) and cathode (pressed  $\text{MnO}_2$ ) are mounted in a plastic cup with a conductive foil, and the assembly is pressed and sealed. Hampartzumian identified the critical design considerations, e.g., stable cell structural materials, reliable air-tight seals, and optimum active cathode formulations necessary to construct a battery of this type for consumer use.

D. Deroo et al. (Domaine Univ.) described a theoretical investigation of the reversibility of lithium intercalation in oxides using an approach reported earlier by S. Atlung et al. (*J. Electrochem. Soc.*, 126 [1979], 1311). The coulombic efficiency of the  $n$ th discharge relative to that of the first discharge was computed for thin films, cylinders, and spherical particles. The coulombic efficiency rapidly levels off. A problem encountered in the comparison of performances for different materials is the lack of uniformity of data. The following parameters need to be established for comparisons: grain size and size distribution, cycling procedure, current density, nominal capacity, and structural aspects such as channel and layer orientation.

Y. Takeda et al. (Mie Univ., Japan) have looked at small cells using chromium oxide cathodes. They examined the series of chromium oxides  $\text{Cr}_3\text{O}_8$ ,  $\text{Cr}_6\text{O}_{15}$ ,  $\text{Cr}_2\text{O}_5$ ,  $\text{Cr}_5\text{O}_{12}$ ,  $\text{CrO}_2$ , and  $\text{Cr}_2\text{O}_3$ ;  $\text{CrO}_3$  was omitted because of its toxicity. The first three are capable of reduction of  $\geq 1$  electron per chromium; the others have somewhat lower capacities.  $\text{Cr}_3\text{O}_8$  is the most promising. Heat treatment of the oxide to 250 to 270°C resulted in optimum performance. Using a propylene carbonate-1,2 dimethoxyethane/lithium perchlorate electrolyte, the heat-treated  $\text{Cr}_3\text{O}_8$  (analysis  $\text{CrO}_{2.55}$ ) cycled 162 times and gave an energy

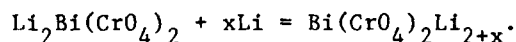
density of 1,170 wh  $\text{kg}^{-1}$  at 500  $\mu\text{Acm}^{-2}$ , based on a 2.0-V cutoff.

S. Narukawa (Sanyo, Japan) described the discharge reactions for the lithium/manganese dioxide, lithium/iron disulfide, and lithium/cupric oxide systems.  $\text{MnO}_2$  undergoes lithium intercalation and reduction to Mn(III) during the discharge. The iron disulfide ( $\text{FeS}_2$ ) and cupric oxide ( $\text{CuO}$ ) cathodes are reduced to the free metals by the lithium.

M. Broussely et al. (Saft-Gipelec, France) described the lithium/AgBi- $(\text{CrO}_4)_2$  battery system. The battery produces 3 V and has a high theoretical energy density. Within the cathode, Ag, Bi, and Cr are reducible. The first step at 3 V is apparently the reduction of Ag and Cr: silver bismuth chromate



where one chromium is Cr(III) and the other Cr(IV). At approximately 2 V the proposed discharge is:



The step is reversible. Some efficiency loss is noted and may be due to the formation of the oxides of Li, Cr, and Bi from the  $\text{Bi}(\text{CrO}_4)_2\text{Li}_{2+x}$  species.

The cells that have been fabricated are small, 0.85 Ah. A 30-year shelf-life has been estimated.

#### Insertion Cathodes

The session on insertion cathodes was devoted to discussions of potential cathode materials other than the oxides. Included were the metal dichalogenides, which have layered structures; intercalated graphite; and polyacetylene. J. Rouxel (Univ. of Nantes, France), presented a comprehensive review of the layer-type electrodes. The materials

exhibit reversible intercalation of metal ions, which retain mobility in the lattice. The electrons that are donated in the process can alter the electronic conductivity of the host. Following intercalation, the host structure relaxes. Coordination of the intercalate can be either octahedral or trigonal prismatic.  $\text{TiS}_2$  exhibits octahedral coordination, niobium disulfide ( $\text{NbS}_2$ ) shows trigonal prismatic, and tantalum disulfide ( $\text{TaS}_2$ ) presents both types. Zirconium diselenide ( $\text{ZrSe}_2$ ) is nominally a semiconductor that undergoes a semiconductor to metal phase transition at 0.4 mole percent intercalate ion. Rouxel is now investigating  $\text{MPS}_3$  compounds.

W.L. Worrell (Univ. of Pennsylvania) continued the session by discussing a thermodynamic model for the variation of lithium chemical potential with composition. Application of the model to  $\text{Li}_x\text{TaS}_2$ ,  $\text{Li}_x\text{TiS}_2$ ,  $\text{Li}_x\text{VS}_2$  gives values for the repulsive interaction energy between intercalated ions of 17.2, 2.9, and 0 KJ mole<sup>-1</sup> ( $\pm 4$  KJ mole<sup>-1</sup>), respectively. The composition variation of the chemical diffusivity (D) was also calculated. The values for  $\text{Li}_x\text{TiS}_2$ ,  $\text{Li}_x\text{TaS}_2$ ,  $\text{Na}_x\text{TiS}_2$ , and  $\text{Na}_x\text{TaS}_2$ , respectively, are approximately  $6 \times 10^{-9}$ ,  $3 \times 10^{-8}$ ,  $1 \times 10^{-9}$  and  $3 \times 10^{-8}$  cm<sup>2</sup>s<sup>-1</sup>. The lithium intercalate values are for the compositional range of x=0 to 1; for sodium, the range is smaller, x~0.3 to 0.6. As expected, there is considerable uncertainty due to the difficulty of defining the electrolyte-solid interface because of electrolyte invasion into the pores.

A. LeMehauté and A. Dugast (Laboratoires de Marcoussis and Univ. of Nantes) discussed a formal theory called TEISI (transfert d'énergie sur interface a similtude interne). Developed at the Laboratoires de Marcoussis by LeMehauté, TEISI was applied to the  $\text{Li}_x\text{FeS}_2$

system. The results were compared with those from experiments with the Li/dioxolane-lithium perchlorate/FeS system. The model yields values for D, the "Hausdorff-Mandelbrot" dimension, of geometry for the interfacial domain. The model and experimental results agree.

There is much interest in the potential application of polyacetylene films as electrode materials. G.L. Farrington (Univ. of Pennsylvania) reported results of experiments on oxidized, or p-doped, polyacetylene. While the experiments were on polyacetylene films supplied by A.G. MacDiarmid (Univ. of Pennsylvania), the work is independent of that of MacDiarmid and A.J. Heeger. The paper generated considerable attention because it is one of the few on the topic to be made public. Several key points were made. The parent polyacetylene is sensitive to oxygen, particularly moist air, and the reaction with oxygen is irreversible. In controlled potential doping experiments, only capacitive charging is noted below about 3.9 V. At 3.9 V the charging current initially grows; it then decreases, but the system continues to exhibit a current draw indefinitely. There was no evidence that the charge was being trapped internally. It was proposed that parasitic side-reactions are responsible for the behavior. The electrochemical behavior is better after an initial charging. Cycling experiments repeatedly gave capacity out figures of 2.0 to 2.2% doping (to 2.5 V). The results were independent of anion ( $\text{AsF}_6^-$ ,  $\text{ClO}_4^-$ ) and doping level. The p-doped films embrittle on cycling, and maintaining electrode integrity was a problem. During the discussion following the paper, Dr. Brummer (EIC Laboratories) said that his organization also had encountered the 2% reversible capacity figure. He pointed out that the anion requirement has a strong detrimental effect on energy density. M. Armand (Domaine Univ.) said that he has doped polyacetylene to about 25% with lithium. The diffusion rate is very low ( $D \sim 10^{-15}$  cm<sup>2</sup>s<sup>-1</sup>).

The other two papers in the session dealt with graphite intercalates. R. Yazami and P. Touzain (CNRS, France) described experiments on the system, Li/polymer electrolyte/carbon. The polymer electrolyte used was poly(ethylene oxide)-lithium perchlorate. The graphite was highly oriented pyrolytic material. The measured Li diffusion coefficient  $D$  for the system operated at  $60^\circ\text{C}$  was  $5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . The free energy was determined to be  $-9.8 \text{ Kcal/lithium}$  for  $\text{Li} + 6\text{C} \rightarrow \text{LiC}_6$ . The latter is a yellow-gold colored material. Yazami and Touzain reported cycling experiments with the latter formulation. The electrode  $\text{LiC}_6$  has a potential of  $340 \text{ mV}$  versus Li when cycled to  $\text{LiC}_{18}$ ; the capacity is  $340 \text{ Ah kg}^{-1}$ . A maximum swelling of 10% is observed.

In the other graphite intercalate paper, Ming-hui Li (Tianjin Institute of Power Sources, China) discussed graphite-antimony pentachloride cathodes. Experiments were performed in propylene carbonate-lithium perchlorate electrolyte. The results as reported are not completely unambiguous. The analysis of x-ray diffraction patterns, lithium content, and the electrochemical data suggest that the process on cycling is not a simple reversible intercalation process. Some reaction between the lithium and  $\text{SbCl}_5$  may occur.

#### Solid Electrolytes

Solid electrolytes for use in lithium battery applications are the subject of considerable investigation. Lithium ion conductors with conductivities comparable to those of nonaqueous solvents are known. There are several materials with the requisite conductivity properties, and many of the important features, such as stability and electrochemical behavior, have yet to be characterized. Because of the potential importance of solid electrolytes, a session of the meeting was devoted to the topic.

Dr. R.A. Huggins (Stanford Univ., US) gave the opening presentation. He reviewed information on some of the known lithium ion conductors and emphasized the thermodynamic requirements for stability. A number of possible electrolytes lack stability toward lithium, for example. It was pointed out, however, that just as passive films permit the use of thermodynamically unstable liquid electrolytes, so might a similar approach be used to extend the solid electrolyte stability range. The  $\text{Li/Li}_2\text{O/LiNO}_3\text{-KNO}_3$  cathode showed how lithium oxide can provide the protective barrier. Huggins also pointed out that it is important to know water's involvement in conductivity because water has a profound effect on conductivity.

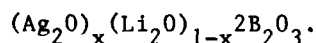
A paper entitled "Lithium-Iodine Cells with Iodine-Polyethylene Oxide Cathodes" was presented by P.M. Skarstad; coauthors were D.R. Merritt, M.S. Norenberg, and R.C. Buchman (Medtronic Energy Technology). Skarstad and his coworkers evaluated cells of the composition  $\text{Li/nI}_2\text{-PEO}$  and  $\text{Li/P2VP/nI}_2\text{-PEO}$ , where PEO is poly(ethylene oxide) and P2VP is poly-2-vinyl pyridine, over an  $\text{I}_2/\text{PEO}$  composition range of 0.13 to 40 moles  $\text{I}_2$  per mole of ethylene oxide. The room temperature conductivity of the mix was  $10^{-6} (\Omega\text{-cm})^{-1}$ . The cells without P2VP had good capacity but gave a low voltage. The 8.0  $\text{I}_2/\text{EO}$  ratio cathode gave the best discharge curve and over 80% utilization.

J.B. Phipps (Northwestern Univ., US) presented some important results on the enhancement of ionic conductivity in lithium iodide by inert oxides. Liang (*J. Electrochem. Soc.*, 120 [1973], 1289) reported that the conductivity of  $\text{LiI}$  increased by two orders of magnitude when particles of alumina were added. Phipps studied such enhancement in the  $\text{LiI.SiO}_2$  systems. He found that the

interfacial conductivity was about  $2 (\Omega\text{-cm})^{-1}$ , whereas the bulk LiI conductivity is  $5 \times 10^{-7} (\Omega\text{-cm})^{-1}$ . The enthalpy of migration is correspondingly less for the interfacial migration process (0.15 eV versus 0.39 eV). As a result, conductivity should be maximized when LiI-ceramic systems are developed containing continuous interfacial transport paths.

B.B. Owens (Medtronic Inc., US) reviewed the development of pacemaker batteries and the lithium-based chemistries now available for them. He stressed the need for high reliability in such batteries. A number of couples have been used; all have energy densities near  $1 \text{ wh-cc}^{-1}$  and 0.2 to  $0.4 \text{ wh-g}^{-1}$ . Lithium-iodine remains the most widely used system. He noted that the first lithium battery was implanted in 1972. Other types of implantable devices are being developed, so there may be increased use of lithium batteries in the human body.

Glassy electrolytes were the subject of the other two papers of the session. G. Robert (Univ. of Besancon, France) discussed LiI in vitreous  $\text{Li}_2\text{S-P}_2\text{S}_5$  supports. The conductivities were about  $10^{-3} (\Omega\text{-cm})^{-1}$  for the bulky glass samples and  $4 \times 10^{-4} (\Omega\text{-cm})^{-1}$  for pressed pellet samples at  $25^\circ\text{C}$ . M. Villa (CNR and the University of Pavia, Italy) reported on mixed cation glasses, specifically



In particular, he and his coauthors have investigated the mixed alkali effects. Using optical and NMR spectroscopy, they showed that the conductivities exhibit a mixed alkali effect. The lithium ions retain some mobility in the silver-ion-rich phases. Thus, the effect is not due to an immobilization of the guest ion. The glass network appears to be more rigid than in either pure phase

( $\text{Ag}_2\text{B}_4\text{O}_7$  or  $\text{Li}_2\text{B}_4\text{O}_7$ ). It is proposed that the effect arises from a dynamic interaction between the mobile ion and the "modes" of the "rigid" lattice.

#### Polymer Electrolytes

Solid electrolytes based specifically on polymers were the subject of a short session. The opening paper by D.F. Shriver (Northwestern Univ.) addressed the mechanism of ion transport in the alkali metal salt-polymer complexes. Shriver's group has established that sodium ion is the predominant mobile species in sodium thiocyanate-poly(ethylene oxide) complexes. There is some evidence that the anion is mobile, but the extent has not yet been established. Shriver reviewed the desirable polymer characteristics for electrolyte formation: high concentration of polar groups, high flexibility (low  $T_g$ ), and low cohesive energy density. In addition, the alkali metal salt should have a low lattice energy. The conductivity data for the ammonium trifluoromethanesulfonate-poly(ethylene oxide) complex shows that the amorphous phase has a higher conductivity than the crystalline phase. Polymer motion is important to the conduction mechanism, and a type of cooperative polymer rearrangement appears to be involved. Some experimental results for lithium and sodium salts of poly(ethylene succinate) were reported. The conductivity for the sodium salt complex is about an order of magnitude less than that for the poly(ethylene oxide)-based system.

A. Hooper (AERE, Harwell, UK) described the fabrication and investigation of lithium cells of the type  $\text{Li}/(\text{PEO})_9 \text{LiSO}_3\text{CF}_3/\text{TiS}_2$  (or  $\text{V}_6\text{O}_{13}$ ). The  $(\text{PEO})_9 \text{LiSO}_3\text{CF}_3$  (lithium trifluoromethane sulfate) composition gives an optimum ionic conductivity; measurements on the system give nearly equal cation and anion transport numbers. The electronic conductivity is at least  $10^4$  times lower. The  $\text{V}_6\text{O}_{13}$  based cell has been cycled over 100

cycles (between 3.2 and 1.8 V) using a  $0.5\text{-mA cm}^{-2}$  discharge current density and a  $0.25\text{ mA cm}^{-2}$  charge current density. The cells are small, with a capacity between 0.2 and 0.3 mAh. Hooper believes that an increase to 1-Ah cells is now possible.

H. Cheradame (Ecole Francaise de Papeterie, France) presented work on ionic conductivity in elastomeric networks of polyether-polyurethane-lithium salt complexes. The complexes exhibit the following properties: for constant T-Tg, the conductivity is proportional to the cation concentration; Tg varies linearly with the salt concentration; the minimum free volume needed for movement of  $\text{Na}^+$  and  $\text{Li}^+$  in PEO-based networks is essentially the same. The authors also concluded that the conductivity is related to chain segment motion.

#### General

The general session included three papers addressing safety-related issues and two on battery systems. A.N. Dey (Duracell International, Inc., US) discussed safety in the lithium-sulfur dioxide system. The key lesson is to "keep the cell cool." The investigation was a differential thermal analysis of the various cell constituents. The presence of moisture causes an exotherm in the lithium bromide electrolyte. Dithionite exhibits a large decomposition exotherm at about  $200^\circ\text{C}$ , giving sulfur as one product. Lithium plus the electrolyte undergoes an exothermic reaction at  $T \geq 170^\circ\text{C}$ . Lithium reacts rapidly at  $T \geq 100^\circ\text{C}$  with acetonitrile. Propylene carbonate gives better safety behavior than acetonitrile, but the performance is poorer after stand. Excess sulfur dioxide can be used to control the thermal reactions.

A. Meitav (Tel-Aviv Univ.) described his work with E. Peled and contrasted their calcium-thionyl chloride system and a lithium-based one. For several years, calcium-thionyl chloride occasionally has been considered as a possible substitute for lithium -

$\text{SOCl}_2$  to avoid some of the safety issues associated with lithium. Experiments were carried out on two test cells,  $\text{Ca/LiAlCl}_4\text{-SOCl}_2/\text{C}$  and  $\text{Ca/Ca(AlCl}_4)_2\text{-SOCl}_2/\text{C}$ . The former gives the  $\text{Li/SOCl}_2$  open circuit voltage on charging, whereas the latter can be taken to 35 V without deposition. This difference in behavior is interpreted in terms of a blocking of the  $\text{Ca}^{2+}$  ionic current through the SEI. It was suggested that the SEI on calcium is an anionic conductor.

W.P. Kilroy (US Naval Surface Weapons Center) presented the results of surface spectroscopic and differential scanning calorimetric analysis of a lithium-sulfur dioxide system. Kilroy's group has found that the lithium surface film contains a number of lithium compounds after exposure to the electrolyte, including several sulfur-containing species. The carbon cathode surface also contains lithium compounds, e.g.,  $\text{Li}_2\text{S}_2\text{O}_4$ ,  $\text{Li}_2\text{SO}_3$ ,  $\text{Li}_2\text{S}$ , and  $\text{LiBr}$ . Dithionite is the principal discharge product under normal discharge conditions. The chemistry is complex under abusive discharge conditions.

L. Werblan (Univ. of Warsaw, Poland) described lithium-cupric sulphide cells. The investigation included methods for preparing the cupric sulphide and selecting the solvent. The solvent chosen was a mixture of equal mole fractions of gammabutyrolactone and 1,2 dimethoxyethane; the electrolyte salt was lithium perchlorate.

In the final paper of the conference, Hai-de Song and Wen-rong Lu (Tianjin Institute of Power Sources, China) described a low-temperature thermal battery based on concepts developed at the US Air Force's Seiler Laboratories. The battery has been designed so that it can be pretested. The active components are a lithium-aluminum alloy anode, a cupric chloride cathode, and a sodium tetrachloroaluminate electrolyte. The actual cathode composition is 58%  $\text{CuCl}_2$ , 16% gra-

phite, and 26% electrolyte by weight. The electrolyte composition is 90% sodium tetrachloroaluminate and 10% silicon dioxide by weight. The electrolyte melting point is 152°C, while the flash point of the zirconium barium chromate pyrotechnic is 200°C. As a result, the battery can be pretested at temperatures less than 200°C without extensive capacity loss or destruction. Pretesting is normally done at 130°C. Pretesting at 175°C produces a 20% loss in capacity after 10 minutes.

Based on the preceding summary, just where does the field of lithium batteries stand now? Certainly one can say that lithium batteries and the associated technology are attracting considerable research and development interest. This is reflected in the number of laboratories and organizations represented at the meeting. The spectrum of potential systems, both primary and secondary, is broadening. Several are now in the commercial marketplace, particularly for the low rate, small capacity applications such as watches, calculators, and certain computer hardware. While this availability may

be good evidence that lithium batteries are here to stay, the long-range commercial future of lithium battery technology continues to be discussed at power source and electrochemical meetings.

There are two reasons for the debate: the safety of large lithium batteries and the practicality of rechargeable lithium systems. The two issues affect a large percentage of the most attractive applications. Both factors were addressed at the meeting. While one cannot draw definite conclusions about the ultimate outcome of efforts to assure the safety of large batteries and to develop rechargeable ones, it is evident that progress is being made on both fronts. The meeting on lithium batteries indicates that there is increasing understanding of the factors contributing to safety. Rechargeable lithium batteries having a practical cycle life (greater than 50 cycles) with reasonable capacity (5 to 20 Ah) have now been built reproducibly.

The Second International Meeting on Lithium Batteries is scheduled for the spring of 1984.

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