A REVIEW OF SILVER, COPPER AND LITHIUM SOLID-STATE POWER SOURCES

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Summary

The most recent developments in silver, copper and lithium solid-state power sources are reviewed. Since the availability of a highly conductive electrolyte plays an important role in the development of the related power source, part of the review is also devoted to the analysis of solid electrolytes either well characterized or still under development, with particular reference to copper and lithium ionic conductors.

Introduction

Solid-state electrochemical devices have been the subject of considerable and constantly increasing attention due to their potential technological applications which range from miniaturized batteries to memory and thermo-electric elements. It appeared of interest therefore to review the latest and most significant achievements in the field and to attempt to forecast its future developments.

A solid-state electrochemical device, such as a battery, implies the use of a solid electrolyte, *i.e.* a solid, generally crystalline, material with a reasonably high conductivity almost entirely due to specific ion movements. Since the availability of such electrolyte plays a key role in the development of the entire device, a large part of this review is devoted to the analysis of the solid electrolytes either known or under development. This analysis has been mainly concentrated on copper and lithium ionic conductors, since the silver ones have been largely discussed in a great number of papers and reviews.

Following each section on the analysis and properties of the electrolytes, there follows a section on the characteristics and the performances of the related solid-state power sources, as well as the possible type of applications.

Silver solid electrolytes

Before entering into the discussion of the properties of solid electrolytes in general it may be useful to point out again that the definition "solid electrolytes" generally applies to those materials characterized by a fast ionic transport associated with a negligible electronic conductivity. As remarked by Geller [1], such a fast ionic transport is generally connected with the nature of a highly disordered structure of the solid.

The first reported material in which these conditions are fulfilled at room temperature is silver rubidium iodide, $RbAg_4I_5$, which was independently discovered by Bradley and Greene [2] and Owens and Argue [3] in 1967. The properties of $RbAg_4I_5$ will not be considered in detail here, since they have already been discussed in various papers dealing with structure [1, 4] thermodynamics [5, 6], transport [7, 8] and applications [7, 9, 10].

The discovery of $RbAg_4I_5$ greatly stimulated the research on silver solid electrolytes and since 1967 a large number of them have been discovered and characterized. All these electrolytes are based on silver iodide to which either large foreign anions or cations have been added in relatively small proportions. Typically these electrolytes, often called of the AgI-substituted type, are prepared by melting a stoichiometric mixture of the two components (or, alternatively, annealing it in the vicinity of the silver iodide $\beta \rightarrow \alpha$ transition point) and then fast cooling the resulting product to room temperature. In certain cases, the preparation is completed by annealing the materials at around 150 °C.

A great number of these electrolytes have been discussed already in various excellent and comprehensive reviews [6, 7, 11] and therefore we will only briefly consider here the class of electrolytes based on the combination of silver iodide with silver oxysalts, which present interesting features in view of practical applications. The properties of typical examples of these electrolytes are reported in Table 1, together with those of $RbAg_4I_5$ for comparison purposes.

It may be noted how the conductivity of silver rubidium iodide, which still remains the solid with the highest ionic conductivity at room temperature, is approximately one order of magnitude greater than that of the silver iodide–silver oxysalt electrolytes. On the other hand, these latter materials exhibit a much higher stability to moisture and iodine at room temperature. This may well counterbalance the lower conductivity for application in practical devices, easily assembled in air and usually based on the Ag/I_2 electrodic couple.

For example, the great stability in moisture of $Ag_7I_4AsO_4$ electrolyte, is shown in Fig. 1, where the time dependence of the resistance of a reciprocal silver/electrolyte/silver cell, kept open in the laboratory atmosphere, is reported. The resistance remains practically constant for a long period of time, showing only casual fluctuations, possibly due to temperature variations [15]. This would not have been the case with $RbAg_4I_5$ which, in the presence of moisture, decomposes below 27 °C into poorly conductive compounds.

TABLE 1

Properties of silver solid electrolytes at 25 °C

|	AgI–Ag$_2$WO$_4$	AgI–Ag$_3$AsO$_4$	AgI–Ag$_3$PO$_4$	AgI–RbI
Reference	[12]	[13]	[14]	[7]
Composition (m/oAgI)	80	80	80	80
Specific conductivity (ohm cm)$^{-1}$	0.047	0.012	0.019	0.24
Activation energy (kcal/mol)	3.6	4.0	3.8	1.7
Electronic conductivity (ohm cm)$^{-1}$	$< 10^{-8}$	$< 10^{-8}$		10^{-11}
Silver transport number	1.00	1.00	1.00	1.00
Decomposition potential (V)		0.68		0.69
Stability in moisture		excellent		poor
Stability in iodine	excellent	good	excellent	bad
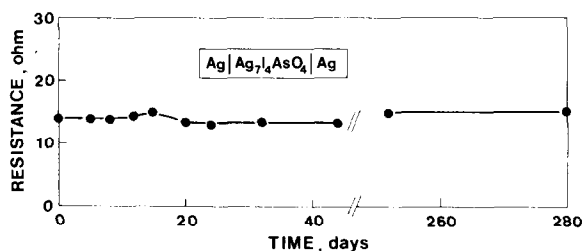
Fig. 1. Time dependence of the resistance of a reciprocal Ag/Ag$_7$I$_4$AsO$_4$/Ag cell at room temperature. Cell surface: 1.2 cm^2. Electrolyte thickness: 0.08 cm.

Also with respect to iodine, the stability of these electrolytes is much greater than that of silver rubidium iodide. This has been clearly shown by Takahaski and coworkers [12, 14] for two typical examples, *i.e.* Ag$_7$I$_4$PO$_4$ and Ag$_6$I$_4$WO$_4$, by measuring the time dependence of the resistance of cells of the type C/electrolyte + I$_2$/C. Their results are summarized in Fig. 2.

The observed high stability to moisture and iodine of the silver iodide–silver oxysalt electrolytes may be possibly correlated to their peculiar structural form. While all the other silver electrolytes are crystalline, the majority of these, and Ag$_7$I$_4$AsO$_4$ and Ag$_7$I$_4$PO$_4$ [16, 17] in particular, show a glass-like structure and may be regarded as supercooled liquids. It is then reasonable to presume that amorphous, glassy materials such as these, are quite insensitive to water and even to iodine.

Furthermore, the possibility of preparing these electrolytes as transparent, highly conductive glasses [17], extends remarkably their interest for suitable technological applications. On the other hand, relevant problems on
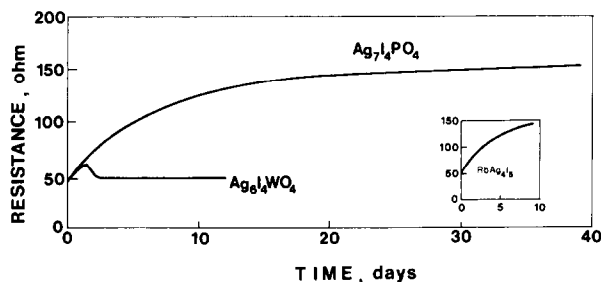
RESISTANCE, ohm

200

150 — $Ag_7I_4PO_4$

100

50 — $Ag_6I_4WO_4$

(inset: 150, 100, 50, 0 — 0, 5, 10 — $RbAg_4I_5$)

0 — 0, 10, 20, 30, 40

T I M E , days

Fig. 2. Time dependence at room temperature of the resistance of cells of the type C/electrolyte + I_2/C, where the electrolyte is $Ag_7I_4PO_4$, $Ag_6I_4WO_4$, and $RbAg_4I_5$, respectively (After T. Takahashi, S. Ikeda and O. Yamamoto, J. Electrochem. Soc., 119 (1972) 477; and 120 (1973) 647.)

these glassy materials are still open. In particular the mechanism of the conduction processes cannot be simply extrapolated from that shown by the tridimensional crystalline solid electrolytes based on AgI, such as $RbAg_4I_5$ and $[(CH_3)_4N]_2Ag_{13}I_{15}$ [1]. Further work is certainly necessary to clarify this point.

Silver solid-state power sources

Silver rubidium iodide has been the electrolyte mostly used in silver batteries. Since the decomposition potential of this electrolyte is around 0.7 V at 25 °C (see Table 1), its use is restricted to those electrode couples whose e.m.f. is less than 0.7 V at the same temperature. Considering the conductive mechanism of this, and generally, of all the silver electrolytes, which is based on transport of silver ions only, one must use silver as the anode. The choice of the cathode has been usually directed towards iodine-based electrodes, since Ag/I_2 is the couple which possesses the highest potential compatible with the electrolyte (0.69 V at 25 °C). Since iodine cannot be used because of its tarnishing action against $RbAg_4I_5$, cathodes with reduced iodine activity have been adopted.

Particularly relevant in this respect has been the work of Owens and coworkers who developed a battery based on the Ag/RbI_3 [7] (or, alternatively, $Ag/(CH_3)_4NI_5$ [18]) couple. The battery fabrication, as well as its performance, has been extensively described by Owens [7]. Here therefore we only summarize the most significant properties in Table 2 and report typical discharge curves in Fig. 3. It may be noted from the data of Table 2 that, even if the electrolyte might suffer a decomposition reaction below 27 °C, these particular batteries (sealed with an epoxy encapsulent [18]) show a very long shelf life. The predicted 10 years seems in fact to be practically achieved on the basis of the results obtained after 5 years storage which indicate no change in the original capacity [18].

Another important feature of the battery, which appears from Fig. 3, is the constant value of the discharge voltage, despite the fact that the product

TABLE 2

Properties of the $Ag/RbAg_4I_5/RbI_3$ solid-state battery at 25 °C [7]

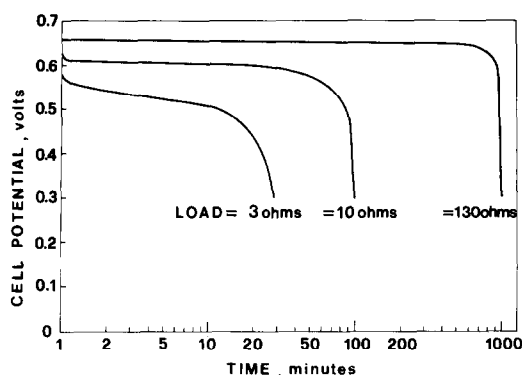|	
Open circuit voltage (V)	0.66
Theoretical specific energy (Wh/kg)	48
Practical specific energy (Wh/kg) (at 25 $\mu A/cm^2$ discharge current density)	4.8
Energy density (Wh/cm^3) (at 25 $\mu A/cm^2$)	0.015
Shelf life (predicted) (years)	10
Shelf life (ascertained*) (years)	5

* For cells using the $Ag/(CH_3)_4NI_5$ couple [18].

Fig. 3. Typical discharge curves at 25 °C of the $Ag/RbAg_4I_5/RbI_3$, C cell. (After B. B. Owens, Advances in Electrochemistry and Electrochemical Engineering, Wiley, New York, 1971.)

of discharge, AgI, has a much lower conductivity than $RbAg_4I_5$. This has been explained, in the case of the $Ag/(CH_3)_4NI_5$ couple [19], by assuming that the silver iodide produced on discharge progressively reacts with tetramethyl-ammonium iodide to form a compound of the type $[(CH_3)_4]_2Ag_{13}I_{15}$, which also is a highly conductive silver double salt [20]. Even if there might be some queries on the kinetic limitations of this proposed reaction at room temperature [21], there are really no other alternatives to explain the flat discharge curves experimentally observed.

This and the long shelf life remain the most interesting features of the silver solid-state batteries but they seem to be insufficient to render them of wide technological interest. The potential and the energetic properties of the system are too low and its cost too high to make it really competitive with more "classical" miniaturized power sources commercially available.

The same drawback also applies to batteries based on silver electrolytes other than $RbAg_4I_5$, as for instance, the silver iodide–silver oxysalt ones previously described. As a typical example, Fig. 4 shows the characteristic curve of $Ag_7I_4AsO_4$, obtained by polarizing in both directions a silver/electro-
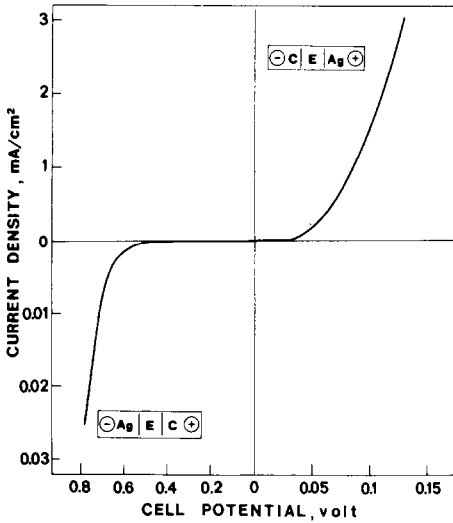
Fig. 4. Characteristic curve at 25 °C of the $Ag_7I_4AsO_4$ electrolyte. (After B. Scrosati, Proc. SAEST, Madras, India, 1976.)

lyte/graphite cell. From the side where the graphite acted as "blocking" electrode [22] for the ionic migration, it may be noted that the electronic conductivity is negligible and that the decomposition potential is again around 0.7 V. This electrolyte is then suitable for use in batteries but also in this case only with couples whose potential is less than 0.7 V at 25 °C.

Considering this limitation, the iodine–phenothiazine (I_2–Ph) charge transfer complex has been selected as cathode material. This complex has proved to be an excellent iodine electrode, both in terms of performance [23] and unreactivity, in connection with silver solid electrolytes in general and $Ag_7I_4AsO_4$ in particular. The latter property is demonstrated in Fig. 5, which shows how the resistance of cells with I_2–Ph as electrode remains practically constant for long periods of time.

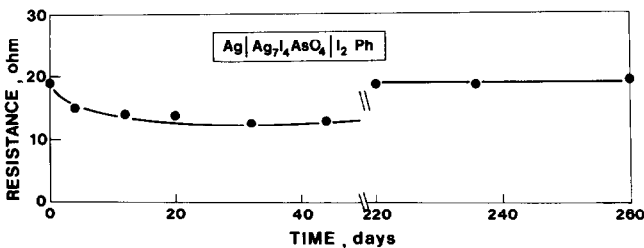Considering these favourable properties, cells of the type:

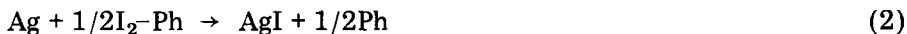$$Ag/Ag_7I_4AsO_4/I_2\text{–Ph} \qquad\qquad (1)$$

Fig. 5. Time dependence at room temperature of the resistance of the $Ag/Ag_7I_4AsO_4/I_2$–Ph cell. Cell surface: 1.2 cm^2. Electrolyte thickness: 0.13 cm.

have been realized and tested [13, 15]. The cells have an open circuit voltage (*OCV*) of 0.615 V at 25 °C, possibly related to the discharge process:

$$Ag + 1/2I_2\text{-}Ph \rightarrow AgI + 1/2Ph \tag{2}$$

A typical polarization curve is reported in Fig. 6 and indicates that cell (1) has a satisfactory electrochemical behaviour since it shows small polarizations even under relatively high discharge current densities. Finally, the properties of cell (1) are summarized in Table 3.

TABLE 3

Properties of the $Ag/Ag_7I_4AsO_4/I_2$-Ph solid-state battery at 25 °C

Open circuit voltage (V)	0.62
Theoretical specific energy (Wh/kg)	48
Practical specific energy (Wh/kg) (at 0.1 mA/cm^2)	1.7
Energy density (Wh/cm^3) (at 0.1 mA/cm^2)	0.013
Shelf life (evaluated)	very long

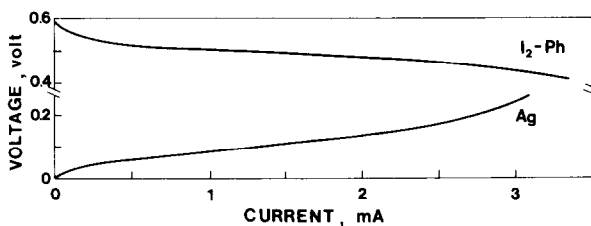
Fig. 6. Polarization curve of the $Ag/Ag_7I_4AsO_4/I_2$-Ph cell at 25 °C. (After B. Scrosati, Proc. SAEST, Madras, India, 1976.)

Also in this case the high volumetric energy density and the long shelf life, when opposed to the low specific energy and high cost, do not seem to suggest a wide range of technological applications for this battery.

The interest in silver solid-state power sources could possibly be stimulated if a fully rechargeable battery were successfully achieved. Detailed studies on the reversibility of silver [24, 25] and iodine [26, 27] electrodes in $RbAg_4I_5$ have been carried out to reach this goal. The results, mainly based on micropolarization and impedance measurements, have shown that both electrodes are indeed reversible with large values of exchange currents.

On the basis of these results, the rechargeability of a silver cell using a typical iodine charge transfer complex as cathode:

$$Ag/RbAg_4I_5/I_2\text{-}Ph \tag{3}$$

was tested [23] by attempting to recharge it from a state of complete discharge, which may be assumed to be:
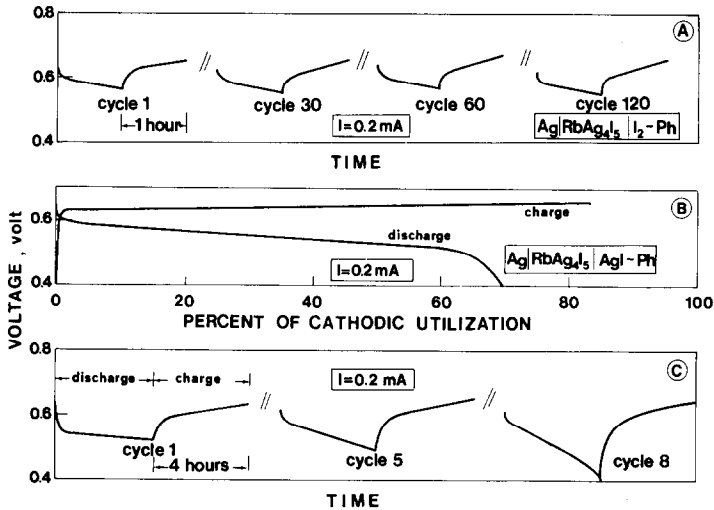
$$Ag/RbAg_4I_5/AgI, Ph \tag{4}$$

Fig. 7. Cycling behaviour of the Ag/RbAg$_4$I$_5$/I$_2$-Ph cell at 25 °C. (After B. Scrosati, Proc. SAEST, Madras, India, 1976.)

Cell (4) can in fact be charged and subsequently discharged with a very good cycling efficiency (about 90%), as shown by the typical cycle of Fig. 7(B).

On the other hand, when the cell, after the initial charge, is submitted to deep charge–discharge cycles, a deterioration readily occurs [15], as shown in Fig. 7(C). This is ascribed to the negative side of the cell, since, as has been largely proved [25, 26, 28], silver undergoes dendritic deposition when a substantial amount of charge is cycled through the electrode/electrolyte interface. Butherus [29] has shown that silver may be cycled in RbAg$_4$I$_5$ repetitively only when the depth of the active silver layer transported does not exceed 0.2 μm. When this depth increases, the number of cycles which result is progressively reduced. Cell (3) may then be regarded as secondary only if limited to shallow cycles, as again indicated by the typical results of Fig. 7(A).

Considering the interest in a fully rechargeable cell, further investigation to explore the possibility of increasing the cycling depth of silver would certainly have important results. One possible direction could be the use of layer-structured materials as silver support in cells of configuration (4). If silver may be intercalated in these materials, one could hope to expand the depth of the interface, thus lowering the tendency of dendritic deposition. Some work in this direction, using transition metal chalcogenides as intercalation electrodes, has been carried out in our laboratories [30] with promising preliminary results.

A similar approach has been used by Takahashi and coworkers [31] who developed a cell of the type:

$$Ag/RbAg_4I_5/\beta\text{-}Ag_2Te \tag{5}$$

The voltage of this cell depends on the deviation from the ideal stoichiometric

composition of silver telluride. It is therefore possible to cycle the cell moving silver in and out of silver telluride. The voltage of the cell (0.120 V at 25 °C as the maximum value) and the cycling regimes (around 50 μA/cm^2) are possibly too low to make it of interest as a practical secondary battery. On the other hand, the fact that the cell, after having been charged to a certain degree, maintains the acquired voltage for a long time, makes it very suitable as a memory element. In fact, the device is now produced commercially for this purpose [32].

In conclusion, one may say that the use of silver solid-state batteries is somewhat limited at the moment by the high cost, low voltage and poor rechargeability. Nevertheless, the great amount of work which has been devoted to the analysis of their properties, remains important for the development of alternative solid-state power sources based on electrolytes with transport via ions of metals less expensive and more energetic than silver, as for instance, copper and lithium. Great research efforts have been polarized in this direction in the latest years and important results have already been achieved. The most significant of these will be discussed in the following sections.

Copper solid electrolytes

Copper solid electrolytes have been recently discovered by Takahashi and coworkers [33, 34] and by Sammels *et al.* [35]. Takahashi has described two classes of compounds based on the combination of cuprous halides with the corresponding halides of *N*-alkyl (or hydro)-hexamethylenetetramine [33] and of *N*, *N'*-dialkyl (or dihydro)-triethylenediamine dihalide [34], respectively. The materials are prepared by annealing the stoichiometric mixtures of the two compounds (or the precipitate obtained by mixing solutions of cuprous halides with those of the organic halides) in a compact form at temperatures slightly below the decomposition point (generally around 150 °C).

Sammels *et al.* [35] have extended the series by examining the compounds resulting from the combination of cuprous halides with quinuclidine, quinuclidinone and pyridinium halides, respectively. The preparation procedure was similar to that used by Takahashi and coworkers. The transport properties of typical examples of these electrolytes, as well as of those reported by Takahashi, are summarized in Table 4.

The compound which has mostly been studied is *N*, *N'*-dimethyl triethylenediamine dibromide—cuprous bromide (TED2CH$_3$Br.CuBr) (94 m/o). Some discrepancy, however, appears in the properties of this material, as reported by various authors. This may be related to the presence of a different amount of unreacted starting materials in the samples examined by the various investigators. It has in fact been ascertained [35 - 37] that the reaction between these starting materials, *i.e.* CuBr and *N*, *N'*-dimethyl triethylenediamine, could proceed to completion only after indefinitely long periods of annealing.

TABLE 4

Properties of some copper (I) solid electrolytes at 20 °C

Electrolyte	Total conductivity (ohm cm)$^{-1}$	Electronic conductivity (ohm cm)$^{-1}$	Activation energy (kcal/mol)	Reference
HMTCH$_3$Br.CuBr(87.5 m/o)	0.017	negligible	4.1	[33]
HMTCH$_3$I.CuI(85 m/o)	0.001	negligible	6.1	[33]
HMTHBr.CuBr(87.5 m/o)	0.006	negligible	4.1	[33]
HMTHCl.CuCl(87.5 m/o)	0.004	negligible	6.2	[33]
TED2CH$_3$I.CuI(85 m/o)	0.002	negligible	4.8	[34]
TED2CH$_3$Cl.CuCl(80 m/o)	0.018	negligible	4.2	[34]
TED2CH$_3$Br.CuBr(94 m/o)	0.035	negligible	2.7	[34]
	0.020*	4×10^{-13}*	4.1	[36]
	0.031	10^{-6}		[37]
	0.002		5.2	[38]
QHBr.CuBr(87.5 m/o)	0.001*		2.7	[35]
QCH$_3$Br.CuBr(87.5 m/o)	0.006*		3.6	[35]
PHBr.CuBr(87.5 m/o)	0.001*		4.2	[35]

HMT = hexamethylenetetramine (C$_6$H$_{12}$N$_4$); TED = triethylenediamine (C$_6$H$_{12}$N$_2$); Q = quinuclidine (C$_7$H$_{13}$N); P = pyridinium (C$_5$H$_5$N). * at 25 °C.

TABLE 5

Structural parameters for some binary salts of the $A^N B^{8-N}$ type [39]

Salt	$(0.79 - f_i)$	ΔG_T(kcal/mol)	T_t (°C)
AgI	0.02	0.5	147
CuCl	0.05	4.5	525
CuBr	0.05	4.5	469
CuI	0.10	8.5	407

Under practical conditions, the X-ray analyses of the final product always show the diffractions of cuprous bromide.

It is also of interest to note from Table 4 that, in contrast to silver conductors, copper solid electrolytes have been obtained by combining the organic halides not only with cuprous iodide but also with cuprous bromide and cuprous chloride. Moreover, the salts derived from these latter two halides have higher conductivities than those based on cuprous iodide, even though the latter has a lower order-disorder transition temperature (see Table

5). A very interesting explanation of this phenomenon has been given by Phillips [39] on the basis of his theory of ionicity [40] for binary compounds of the $A^N B^{8-N}$ type (*e.g.* AgI, CuCl, CuBr, CuI, *etc.*). According to this theory, the energies related to covalent and ionic bonds in these compounds may be determined spectroscopically and their values furnish the possibility of determining the free energy differences, ΔG_T, between the two possible configurations they can assume, *i.e.* those of four-fold and six-fold coordination. When displayed in covalent–ionic plane, the compounds with four-fold coordination are separated from the six-fold coordinated ones by a line at a critical value of ionicity equal to 0.785. The closer the value of the ionicity, f_i, of a given compound is to this critical value, the lower will be the Gibbs free energy difference, ΔG_T, between the four-fold and the six-fold coordinated structure.

As may be seen from Table 5, a salt which is very close to this condition is silver iodide. When a foreign ion is added to AgI (or, generally, to a $A^N B^{8-N}$ salt with a ΔG_T value near zero) and the mixture is brought to a temperature near or above the phase transition, T_t, where presumably the Ag (or generally A) ions are separated from the I (or generally B) partners, a double salt is formed with a "scaffolded" [39] structure which results as a compromise between the two possible coordination configurations which AgI (or generally $A^N B^{8-N}$) may assume. These scaffolded structures may be regarded as formed by a skeletal framework of minority cation complexes (*e.g.* RbI_6 in $RbAg_4I_5$) decorated by loosely bound, quasi-interstitial majority cations (Ag) [39]. This would account for the relative easiness of obtaining double salts from AgI and their high conductivity.

When cuprous halides are considered, one may note from Table 5 that the chemical bonding parameters $(0.79 - f_i)$ and the free energy differences (ΔG_T) between the two coordinations are both lower for CuBr and CuCl than for CuI. It is then reasonable to expect, as pointed out by Phillips [39], a consistent sequence for the conductivity of the related double salts, as in fact, has been found experimentally.

Furthermore, the greater difference in coordination energy values with respect to silver iodide accounts for the necessity of using larger minority substituting ions for the stabilization of comparable disordered structures. In fact attempts to obtain stable cuprous double salts with substituting ions of the type used in the case of silver iodide have not been successful. A possible exception could be KCu_4I_5. It is interesting to note, however, that this salt is stable only in a very narrow temperature range, *i.e.* between 257 °C and 332 °C, as reported by Bradley and Greene [2] and recently verified by Bonino and Lazzari [41].

Beside the copper solid electrolytes described above, other materials with a certain conductivity via copper ions in the solid state are known. One of these, discovered by Ketelaar as far back as 1934 [42], is Cu_2HgI_4. This salt undergoes at a relatively low temperature (about 70 °C) a $\beta \rightarrow \alpha$ phase transition, accompanied by a change in colour and a jump in conductivity of approximately two orders of magnitude [42, 43]. The α-phase, stable at high

temperature, has a relatively disordered structure based on a face-centred cubic arrangement of anions with the cations randomly distributed in the interstices [44], which accounts for the fairly good conductivity (about 10^{-5} ohm^{-1} cm^{-1} at 70 °C).

Despite this and the possible specific applications related to its peculiar properties (thermoconductivity and thermochromicity) there has not been further substantial investigation on Cu_2HgI_4 since the work of Ketelaar. This is possibly related to the fact that it has often been assumed that the transport in cuprous salts was mostly electronic. Recent work on cuprous halides [45, 46] and on Cu_2HgI_4 [47] in particular, mainly based on Wagner's analysis [48], has instead shown that cuprous salts, when not contaminated by Cu(II) impurities, may be good ionic conductors. On the basis of this, it appears now that Cu_2HgI_4 could be an interesting materials for basic and applied work.

Another class of copper solid conductors of the CuTeX type, where X may be Cl, Br and I, respectively, has been recently reported by Rabenau *et al.* [49, 50]. By electrochemical analyses, based on copper transference number, polarization and a.c. conductivity measurements, the authors have shown how the materials may be regarded as good copper conductors at moderately high temperatures. In fact, at 200 °C the total conductivity of CuTeBr and CuTeCl is of the order of 0.01 (ohm cm)$^{-1}$ with an almost negligible electronic contribution, *i.e.* of the order of 10^{-8} (ohm cm)$^{-1}$. Preliminary tests on the compatibility of the bromide and the chloride salts with copper, indicated that these compounds may be considered for practical uses, such as in copper solid-state devices.

Copper solid-state power sources

Amongst the various copper solid electrolytes so far reported, the N, N'-dimethyl triethylenediamine dibromide–cuprous bromide at 94 m/o (TED2CH$_3$Br–CuBr), is the one which has received most attention in view of practical applications. In fact, this material, if prepared and kept under dry conditions [51], has a very high conductivity (about 0.03 ohm^{-1} cm^{-1} at room temperature) which is prevalently ionic in character [34, 36]. Studies on the properties of this material have shown its incompatibility with the most common halogen electrodes [36] and that its decomposition potential is around 0.7 V at 25 °C. Furthermore, studies reported by Armstrong *et al.* [37] have shown a very low value of exchange current for the copper electrode in this electrolyte. The utilization of TED2CH$_3$Br–CuBr in copper power sources would then imply the use of electrode couples whose e.m.f. is less than 0.7 V at 25 °C.

Considering this limitation and the fact that the anode must be copper because of the conduction mechanism of the electrolyte (exclusively via copper ions), non-stoichiometric and layer-structured materials have been considered as possible cathodes. Amongst these, $Cu_{1.8}S$ and TiS_2, have been
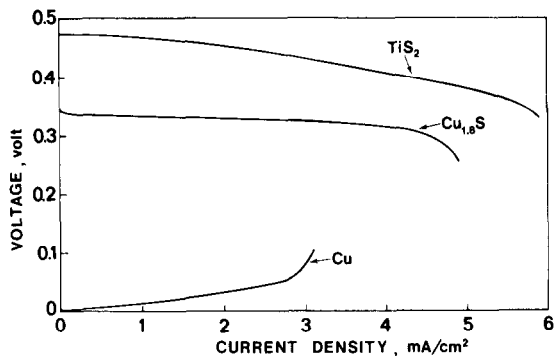
Fig. 8. Polarization curves of the Cu, TiS_2 and $Cu_{1.8}S$ electrodes in $TED2CH_3Br-CuBr$ electrolyte at 25 °C. (After M. Lazzari, G. Razzini and B. Scrosati, J. Power Sources, 1 (1976) 57.)
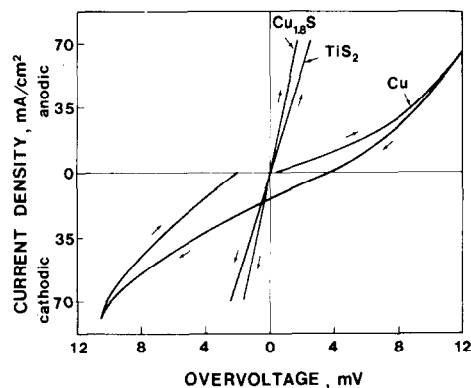
Fig. 9. Micropolarization tests for the Cu, TiS_2 and $Cu_{1.8}S$ electrodes in $TED2CH_3Br-CuBr$ electrolyte at 25 °C. (After M. Lazzari, G. Razzini and B. Scrosati, J. Power Sources, 1 (1976) 57.)

shown [51] to behave satisfactorily in terms of stability and polarizability. In fact the potentials of $Cu/Cu_{1.8}S$ and Cu/TiS_2 couples in $TED2CH_3Br-CuBr$ are 0.34 and 0.47 V, respectively at 25 °C, and their polarization curves are reported in Fig. 8. It may be noted that the higher polarization is shown by the copper electrode, in agreement with the work of Armstrong *et al.* [37] in which the slow charge transfer reaction of the Cu/Cu^+ electrode was pointed out. This is also confirmed by reversibility studies on the three electrodes carried out with micropolarization measurements, the results of which are shown in Fig. 9 [51]. In the case of TiS_2 and $Cu_{1.8}S$ the anodic and the cathodic runs lie on a straight line, while for the copper electrode the micro-polarization traces show a definite effect of hysteresis.

It therefore appears that titanium disulphide and non-stoichiometric copper sulphide may be considered as very promising cathodic materials for reversible copper solid-state power sources based on the $TED2CH_3Br-CuBr$

electrolyte. Eventual failures in these cells may be ascribed to the poor kinetic properties of the copper electrode.

To confirm this, rechargeability tests have been carried out on cells of the type:

$$Cu/TED2CH_3Br-CuBr/Cu_{1.8}S(or\ TiS_2) \tag{6}$$

by submitting them to charge–discharge cycles at 0.2 mAh [51]. The results, reported in Fig. 10, indicate a very good efficiency in the first cycles but also a progressive cell deterioration between the 10th and the 20th cycle.
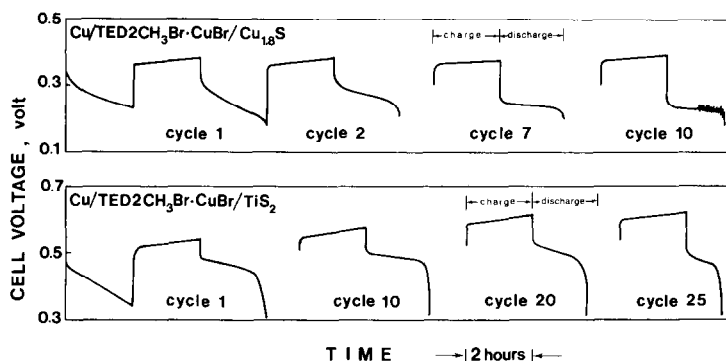

Fig. 10. Cycling behaviour at 0.2 mAh for cells of type (6) at 25 °C. (After M. Lazzari, G. Razzini and B. Scrosati, J. Power Sources, 1 (1976) 57.)

Such a cycling failure, very likely to be ascribed to the copper electrode, has also been noticed by Sammels et al. [35] in cells using other copper solid electrolytes. In fact, these authors, examining the cycling behaviour of the cell

$$Cu/PHBr-CuBr/C \tag{7}$$

where PHBr stands for pyridinium bromide, noticed a progressive deterioration, in terms of charge–discharge efficiency, within 7 cycles.

Considering the above results, it would seem opportune to test other copper solid electrolytes and/or to develop alternative copper electrodes. Very recently, Takahashi and Yamamoto [52] have described the properties of cells based on the $HMTCH_3Br-CuBr$ electrolyte (see Table 4). The decomposition potential of this electrolyte was found to be 0.83 V at 25 °C. Considering this value, the authors [52] selected the following system:

$$Cu/E/X,\ Cu_2X,\ C \tag{8}$$

where E stands for the $HMTCH_3Br-CuBr$ electrolyte and X in turn for S, Se or Te. The OCV values, related to the electrochemical reaction:

$$2Cu + X \rightarrow Cu_2X \tag{9}$$
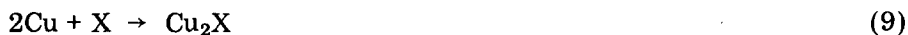
result at 25 °C in 0.448, 0.373 and 0.258 V, respectively. The anodic and
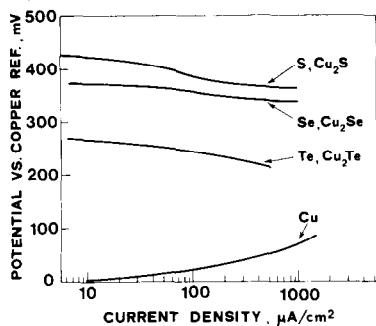
Fig. 11. Polarization curves of the Cu, S, Se and Te electrodes in the HMTCH₃Br–CuBr electrolyte at room temperature. (After T. Takahashi and O. Yamamoto, J. Appl. Electrochem., 7 (1977) 37.)

cathodic polarization curves at room temperature are shown in Fig. 11. From these curves it appears that also in this case the systems are limited by anodic polarization [52]. Finally, the properties and the performance of cells of type (8) are summarized, in the case of the Cu/Se couple, in Table 6.

The results described indicate that, even if the cost of the copper solid-state power sources is certainly much lower than that of silver ones, the energy and rechargeability characteristics are comparable and therefore still too poor to open wide ranges of applicability. The need for the development of alternative solid electrolytes which would allow the realization of high voltage solid-state batteries, such as for instance those based on lithium transport, is at the moment strongly felt. The most recent results obtained in this direction will be discussed in the next section.

TABLE 6

Properties and performance of the Cu/HMTCH₃Br.CuBr/Se solid-state battery at 25 °C and 50 $\mu A/cm^2$ discharge current density [52]

Open circuit voltage (V)	0.37
Cut-off voltage (V)	0.26
Capacity (mAh)	26
Practical specific energy (Wh/kg)	4

Lithium solid electrolytes

Various materials have been described as solid conductors with fairly good lithium ionic conductivity at room or moderately high temperature. As suggested by Pizzini [53], these materials may be subdivided into three main

groups, namely: (a) compounds where Schottky defects prevail, such as lithium halides; (b) polymorphic compounds where Frenkel defects are predominant, such as lithium sulphate or similar oxysalts; (c) anisotropic compounds with layer or tunnel structure, such as lithium beta-alumina.

The early stage of the study of lithium solid conductors for practical applications was mainly directed towards the investigation of the properties of the first group of compounds and, in particular, of lithium iodide. This material has a rocksalt type structure with a limited number of Schottky defects through which the cation transport takes place via a hopping mechanism. The intrinsic conductivity of LiI is very low at room temperature, *i.e.* of the order of 10^{-7} (ohm cm)$^{-1}$.

A systematic work directed to enhance this conductivity by doping or incorporating foreign ions in LiI has been carreid out by Liang and coworkers. Their results have been extensively reported and discussed in various reviews [54 - 56] to which the reader is referred for detailed information. Here the values of the conductivity of the various materials obtained, which are summarized in Table 7, will be briefly commented upon.

TABLE 7

Specific conductivity of lithium solid conductors based on LiI

Conductor	Temperature (°C)	Ionic conductivity (ohm cm)$^{-1}$	Reference
LiI	25	1.2×10^{-7}	[57]
LiI(CaI$_2$, 0.4 m/o)	28	2.6×10^{-6}	[58]
4LiI.NH$_4$I	25	2.0×10^{-6}	[59]
LiI(Al$_2$O$_3$, 33 - 45 m/o)	25	10^{-5}	[60]

The increase in conductivity of LiI obtained by doping with CaI$_2$ is somewhat difficult to interpret. In fact, while it is known that divalent cation doping induces defects in the crystal lattice of the majority of lithium halides [61], this seems not to be the case for LiI [53, 61]. The much greater increase observed for the lithium iodide–aluminium oxide material (see Table 7) cannot then by any means be explained by a classical doping mechanism, as was also pointed out by Liang [60]. No mutual solubility or compound formation was reported for this material but rather an activation energy and conduction mechanism identical to those of pure lithium iodide [60]. One may then consider that, if LiI has an enhanced defect concentration near its surface, as is often assumed [62], the incorporation of foreign substances may serve to enlarge the internal surface area, thus enhancing the grain boundary conductivity.

The group (b) compounds are of great interest insomuch as they undergo a phase transition accompanied by a great structural disorder. In this respect

it is remarkable that in some of these compounds, as for instance Li_2SO_4, the heat of transition is much higher than the heat of melting, thus showing a considerable entropy change in passing from the low to the high temperature phase. The structure of this latter may be described in terms of sulphate ions arranged in a face-centred cubic lattice in which both tetrahedral and octahedral positions are available for the cations [63]. The large excess of these positions explains the high cation mobility and makes the α-phase of Li_2SO_4 a highly conductive lithium solid electrolyte.

Various attempts have been made to lower the conductivity range of Li_2SO_4 and other compounds of this group. Kvist and Bergtzelius [64] have found that a large number of binary systems based on Li_2SO_4 (a typical example being $LiAgSo_4$) show extended regions with high ionic conductivity (Fig. 12). The transport is, however, of the cumulative type in the sense that both lithium and the added foreign ion are mobile in the sulphate systems [64, 66, 67]. This applies to a great variety of ions and has been explained by the assumption that in pure Li_2SO_4 the sulphate ions are partly free to rotate. The addition of another component provokes a change in the rotational properties with a consequent deformation of the lattice which allows the transport of the new species [64].
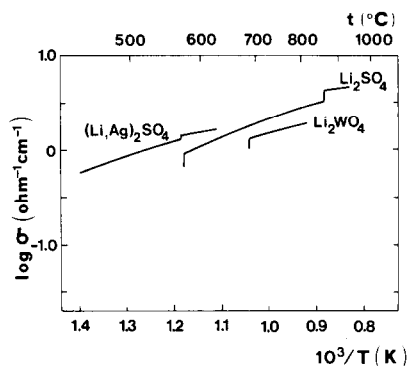

Fig. 12. Conductivity of Li_2SO_4, Li_2WO_4 and $LiAgSO_4$. (After A. Kvist and A. Lundén, Z. Naturforsch., 21a (1966) 1509.)

Recently, West [69] has reported the results of a detailed study on the properties of lithium silicate and its solid solutions with various salts. Also Li_4SiO_4 exists in two polymorphic forms separated by a rather broad transition region between 600 °C and 725 °C, which seems to occur in several successive stages (see also Table 8, where the conductivity values of group (b) compounds are summarized). The structure of Li_4SiO_4 may be simply described in terms of SiO_4^{4-} tetrahedra linked by 8 lithium ions, per unit cell, distributed over 18 possible sites. This accounts for the fairly good conductivity of Li_4SiO_4 at moderately high temperatures. Moreover, the conductivity may be remarkably increased by replacement of silicon with titanium up to a maximum of 40% of substitution, as found by West [69]. In fact, the com-

TABLE 8

Conductivity of lithium solid conductors based on Li_2SO_4, Li_2WO_4 and Li_4SiO_4

Salt	Specific conductivity $(ohm\ cm)^{-1}$	Temperature (°C)	Reference
Li_2SO_4	1.0	572	[68]
	3.0	850	[68]
Li_2WO_4	1.25	684	[65]
Li_4SiO_4	10^{-5}	300	[69]
	0.001	400	[69]
	0.01	600	[69]
$Li_4(Si_{0.6}Ti_{0.4})O_4$	0.001	300	[69]
$Li_4SiO_4.0.43Li_3PO_4$	4.5×10^{-7}	25	[70]
	1.6×10^{-3}	200	[70]
	0.092	400	[70]
$Li_{3.75}Si_{0.75}P_{0.25}O_4$	0.001	200	[72]
	0.01	300	[72]
$Li_{4.4}Si_{0.6}Al_{0.4}O_4$	7.6×10^{-4}	200	[72]
	0.008	300	[72]
$Li_{3.4}Si_{0.7}S_{0.3}O_4$	0.001	200	[72]
	0.01	300	[72]
$Li_{2.25}C_{0.75}B_{0.25}O_3$	0.001	200	[72]
	0.01	300	[72]
$LiAlSiO_4$	0.001	300	[73]
	0.01	400	[73]

TABLE 9

Transport properties of polycrystalline Li/Na beta alumina at 25 °C [77]

Specific conductivity $(ohm\ cm)^{-1}$	5×10^{-3} (intergranular)
	1×10^{-3} (bulk)
Activation energy (kcal/mol)	4.6 (intergranular)
	7 (bulk)
Lithium transport number	nearly one
Electronic conductivity	negligible

pound with the composition $Li_4(Si_{0.6}Ti_{0.4})O_4$ has at 300 °C a conductivity of 10^{-3} $(ohm\ cm)^{-1}$, a value of great interest when compared with those of other known lithium conductors (see Tables 7 - 9).

The results of West have stimulated further investigation on alternative Li_4SiO_4 solid solutions with the aim of finding other low temperature lithium solid electrolytes. Particularly relevant in this respect are the results of Huggins and coworkers and of Shannon and coworkers. In a recent symposium Huggins [70] has reviewed the work carried out in his laboratory and reported that an improvement of 3 to 4 orders of magnitude in conductivity is obtained when Li_4SiO_4 is added to Li_3PO_4 to form a solid solution in which part of the SiO_4 tetrahedra is replaced by PO_4 tetrahedra. Typical values of conductivity of the solid solution at 43% of Li_3PO_4 are reported in Table 8 and in Fig. 13.
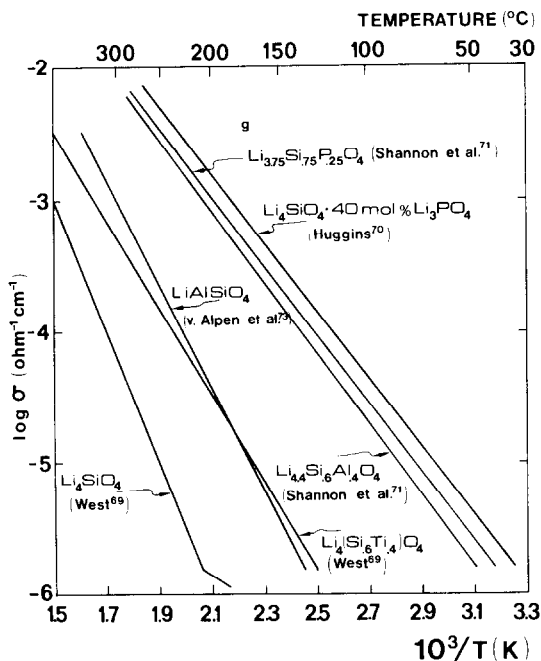

Fig. 13. Conductivity of various lithium solid conductors based on Li_4SiO_4.

Similar results have been obtained by Shannon who, in the same symposium [71], described the great improvement in the conductivity of Li_4SiO_4 obtained by substitution with a series of lithium oxysalts, amongst which were phosphates, aluminates and sulphates. This increase in conductivity has to be related to the extra Li vacancies and interstitials produced in the original structure by the substitution. Typical values of the conductivity of the most representative lithium conductors found by Shannon and coworkers [72] are reported in Table 8 while in Fig. 13 is shown the temperature dependence of the conductivity of $Li_{3.75}Si_{0.75}P_{0.25}O_4$.

The properties of another lithium aluminium silicate, *i.e.* $LiAlSiO_4$ have been examined by von Alpen *et al.* [73]. The results of these authors have shown that the material is a one-dimensional lithium ionic conductor with a

conductivity, parallel to the c-axis, which is comparable with that of other conductors based on lithium silicate, as again shown in Fig. 13 and Table 8. Examination of this Table indicates that, even if a lithium solid electrolyte with a conductivity at room temperature of the same order as that of the silver and copper ones has not yet been found, sensible progress has been achieved by the systematic research carried out lately on the lithium silicate materials. In particular, the compounds reported by Huggins and Shannon appear to be of technological importance since they may be sintered in the form of dense, stable ceramic materials of easy manipulation.

For similar reasons, lithium beta alumina may be considered of comparable interest. The substitution of sodium by lithium in beta alumina was first reported by Yao and Kummer [74] who found that the exchange process in molten $LiNO_3$ at 350 °C was limited to approximately 50%. This result has been recently confirmed by Farrington and Roth [75] after a thorough re-investigation of the sodium–lithium exchange process.

The most remarkable property of the Li/Na beta alumina is that lithium ions can move through it without significantly affecting the Li^+/Na^+ ratio. This phenomenon, termed "co-ionic conductivity" [76], has been explained by assuming that the two mobile species are not randomly distributed in the conductive planes of beta alumina but rather that there is a preferential occupation of specific sites by specific ions and that they do not interfere in the transport processes [77]. This appears a very reasonable explanation since there are three non-equivalent crystallographic sites in the conductive planes of beta alumina and, as pointed out by Yao and Kummer [74], lithium ions seem to be preferentially located in off-centre positions, with respect to sodium, in these planes.

It is interesting to note that Farrington and Roth retained that co-ionic conductivity could possibly not be limited only to beta alumina but rather be regarded as a general phenomenon in open-structured solid conductors. As support to this statement, it is perhaps significant to cite recent results obtained in our laboratories on the substitution of silver by copper in AgI-modified electrolytes [78]. In this case the degree of substitution was modest, i.e. 0.35 and 0.70% of silver by weight could be replaced by copper at 25 °C and 70 °C, respectively. After saturation was reached, however, the electrolytes behaved as copper conductors and the migration of copper ions did not substantially alter the Ag/Cu ratio, a behaviour which is indeed qualitatively similar to that of Li/Na beta alumina.

This latter material, as the above considerations indicate, may then be practically considered as a lithium solid conductor and its transport properties are summarized in Table 9.

Lithium solid-state power sources

There has been in the latest years a massive development of miniaturized electronic devices which have reached a predominant role in various applied

fields. Typical examples are cardiac pacemakers and electric watches. The majority of these devices are still powered by conventional "dry" batteries but their performance would be greatly improved if a power source characterized by absence of gassing and leakage, long service life and stability, high voltage and energy density, could be used as an alternative.

It is obvious how a lithium solid-state battery with a reasonably low internal resistance would entirely fulfill these requirements and this accounts for the large research efforts recently directed to accomplishing the development of such a battery.

Various lithium solid power sources which have already reached the stage of commercial prototypes have been systematically tested by Feister *et al.* [79] and by Owens [80, 81], especially in view of their utilization in cardiac pacemakers. In this respect two systems appear of interest and they are both based on LiI as electrolyte. The first, developed by Liang and coworkers [82], utilizes $LiI(Al_2O_3)$ as electrolyte [60] and a PbI_2–PbS mixture as cathode, according to the basic structure:

$$Li/LiI(Al_2O_3)/PbI_2, PbS \tag{10}$$

The cell is assembled in a controlled environment, by pressing its components into a single pellet retained by a polypropylene ring and hermetically sealed in a steel battery housing [82]. The *OCV* of the cell, based on the reactions:

$$2Li + PbI_2 \rightarrow 2LiI + Pb$$

$$2Li + PbS \rightarrow 2Li_2S + Pb \tag{11}$$

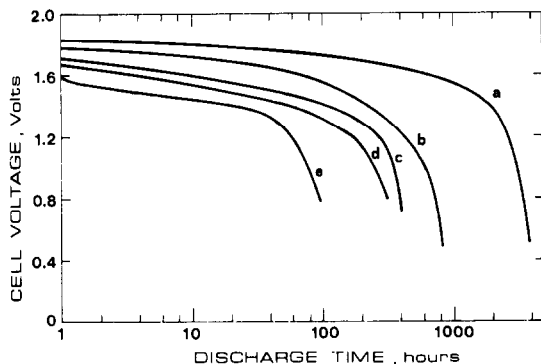is 1.91 V at 25 °C. Typical discharge curves at room temperature, for a 136 mAh cell, are shown in Fig. 14.

Fig. 14. Typical discharge curves of a 136 mAh $Li/LiI(Al_2O_3)/PbI_2$,PbS cell under various constant currents and at room temperature. (a) 18 μA; (b) 36 μA; (c) 54 μA; (d) 72 μA; (e) 90 μA. (After C. C. Liang and L. H. Barnette, J. Electrochem. Soc., 123 (1976) 453.)

Discharge and storage tests, obviously directed to the investigation of applicability in implantable pacemakers, have also been conducted at 37 °C for various series and parallel combinations. In Table 10 are summarized the

TABLE 10

Initial properties of the Li/LiI(Al_2O_3)/PbI_2,PbS solid state battery at 37 °C

	Liang and Barnette [82]	Owens et al. [81]
Open circuit voltage (V)	6	6
Load current (μA)	~ 2	15.5
Load voltage (V)	above 5	5.64
Internal resistance (ohm)		400
Rated capacity (Ah)	0.14	1.1
Cell configuration	3, series	3, series x 8, parallel
Cell surface (cm^2)	1.5	
Energy density (Wh/cm^3)	0.49	0.44
Shelf life (years) (tested)	1	
(estimated)	very long	

initial properties of two of these combinations, as determined by Liang and Barnette [82] and Owens et al. [81]. The first authors [82] reported that after two years of low drain discharge the load voltage was still above 5 V, thus implying that the battery could fulfill the standard pacemaker requirements. Comparable tests performed by Owens and coworkers [81] and by Feister and coworkers [79] indicated that the internal resistance continuously increased during discharge to reach twice its initial value after three years of service. The load voltage decreased accordingly and therefore these authors predicted that the battery would reach the cut-off voltage limit, established by normal pacemaker requirements, after having delivered 50% of the rated capacity [81]. On the other hand, complete real discharge tests of this system, as well as of others under similar examinations under simulated conditions of a pacemaker drain (about 10 μA for 7 years), have not yet been accomplished [80, 81]. The conclusions on their performances are based on extrapolated or accelerated discharge curves and have therefore to be regarded with a certain degree of uncertainty.

Another lithium solid-state battery commercially available has been realized by Schneider and coworkers [83, 84]. The cell is obtained by directly contacting a lithium anode with a cathode formed by the poly(2-vinylpyridine)–iodine (P2VP.nI_2) charge transfer complex. As already pointed out, iodine charge transfer complexes behave as iodine electrodes with reduced iodine activity [23] and therefore, by contacting one of these with lithium, an immediate reaction with the formation in situ of a thin layer of LiI (which in turn acts as electrolyte) takes place.

The concept of realizing low internal resistance batteries with this procedure is not new. It was first adopted by Gutmann and coworkers [85] to

realize Mg/I_2 cells and then utilized by various authors for a series of systems [55], amongst which was also Li/I_2, obtained using iodine–benzidine as a charge transfer complex electrode [86]. The magnesium cell, however, appeared unable to operate except in the presence of traces of water or other high permittivity solvents, probably because they partially dissolved the electrolyte, thus increasing its conductivity [55]. In the case of the Li/I_2 system, it was noticed that the cell resistance, even if low initially, constantly increased under open circuit conditions, as a result of the diffusion of iodine through the LiI, which produced a continuous build-up of the separation layer [86].

This does not appear to take place in the system developed by Schneider where self-discharge losses have been estimated to be less than 10% over a period of 10 years [84]. The basic structure of Schneider's system is:

$$Li/LiI/P2VP.nI_2 \tag{12}$$

with an *OCV* of 2.80 V at room temperature, related to the electrochemical reaction

$$2Li + P2VP.nI_2 \rightarrow P2VP(n-1)I_2 + 2LiI \tag{13}$$
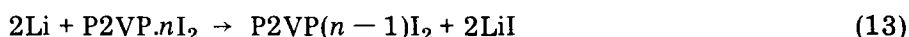
The construction of the battery is described in detail in various papers by Schneider and coworkers [84, 87]. A typical discharge curve at 37 °C, partly based on accelerated tests, is shown in Fig. 15. The long shelf life and the relative flatness of the discharge curves make this battery particularly suitable for applications in pacemakers and similar devices [87], as also apparently do its general properties which are summarized in Table 11.

TABLE 11

Initial properties of the $Li/LiI/P2VP.nI_2$ solid-state battery at 37 °C

	Schneider *et al.* [84]	Owens *et al.* [81]
Open circuit voltage (V)	2.80	5.60
Load current (μA)	28	14
Load voltage (V)	2.78	5.58
Projected (6 years) load voltage (V)	2.60	
Internal resistance (ohm)	~ 600	50
Rated capacity (Ah)	3.5	1.1
Cell configuration	double anode, single cell	2, series
Cell surface (cm^2)	25	
Energy density (Wh/cm^3)	0.30	0.44
Shelf life (estimated) (years)	> 10	

CAPACITY CONSUMED, Ah
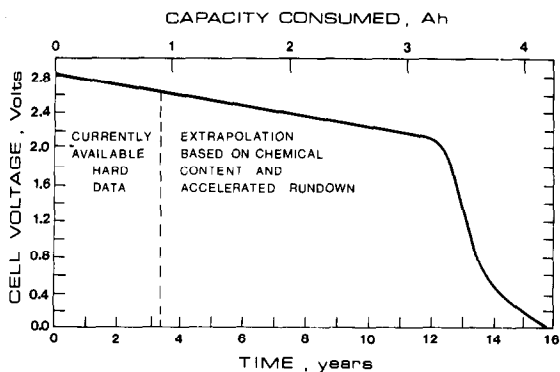

Fig. 15. Discharge curve of a Li/LiI/P2VP.nI$_2$ cell at 37 °C under 30 μA load. (After A. Schneider, W. Greatbach and R. Mead, in D. Collins (ed.) Power Sources 5, Academic Press, London, 1975.)

Besides the two examples described above, there are other lithium solid-state batteries either still under study or in a preliminary development stage. Those still based on LiI and related double salts (see Table 7) have been discussed extensively by Liang [54, 88]. A number of systems using lithium sulphate as electrolyte have been reported by Buzzelli in a series of patents [89]. These systems use lithium or lithium alloys as anodes and various transition metals and their oxides as cathodes. The operability of the battery is restricted to a temperature range between 575 °C and 870 °C, *i.e.* from the transition to the melting point of Li$_2$SO$_4$. Nevertheless the work of Buzzelli shows the applicability of lithium sulphate, and probably of other lithium oxysalts, as an electrolyte for solid-state power sources. It may then be presumed that the recent discovery of the highly conductive materials based on Li$_4$SiO$_4$ will stimulate the development of batteries capable of operating at medium temperatures, as well as the research on other classes of solid ionic conductors.

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