

LITHIUM-CUPRIC SULFIDE CELLS

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(Received June 23, 1982)

Summary

Results for the preparation and properties of cupric sulfide electrodes prepared by two different methods are given. Details concerning the chemical composition, the porosity, and the structure of the sulfide electrode are presented.

Problems related to the selection of appropriate organic solvents and electrolyte solutions in order to determine those which would be compatible with the electrode materials (Li/CuS), and would also secure the best conditions for transport of charge and mass through the solution, are presented. The following solvents and their mixtures were tested: gammabutyrolactone (gBL), tetrahydrofuran (THF), 1,2-dimethoxyethane (1,2-DME), 1,1-dimethoxyethane (1,1-DME), and two component mixtures of gBL with 1,2-DME and gBL with 1,1-DME.

Transport phenomena — the electrical conductivity and viscosity of lithium perchlorate solutions in these solvents were measured. A laboratory technology for the construction of a Li/CuS cell has been developed.

1. Introduction

In this paper we present the results of our research on the electrode system consisting of a lithium anode and a cupric sulfide cathode (Li/CuS). The system Li/CuS has a sufficiently high theoretical specific energy value of *ca.* 1100 W h/kg [1] to be of interest for many cell applications.

Cupric sulfide is a valuable cathode material, since it is stable, chemically inert, and provides no environment risk. Moreover, its reaction products with lithium are also quite safe, and both copper and sulfur are cheap and readily available.

Cupric sulfide is a semiconductor insoluble in water and organic solvents; the latter property is particularly important in the application of semiconductors to the construction of batteries. Gabano [2, 3] and Dampier

[4] studied the system. THF with 1,2-DME was used as a solvent, although according to other reports THF dissolves metallic lithium [5].

2. Electrolyte properties and cathode preparation

In our investigations [6] we focussed our attention on the choice of the best compatible electrolyte solutions and on the preparation and structure of the cathode material.

The electrolyte solution should provide the correct conditions for charge and mass transport and for the satisfactory passivation of the lithium electrode in an organic solvent of the solute.

The preparation of the cathode material is fundamentally important because it determines the efficiency of the lithium electrode and the power output of the cell.

The following solvents were chosen: gammabutyrolactone (gBL), tetrahydrofuran (THF), two isomers — 1,2-dimethoxyethane (1,2-DME), 1,1-dimethoxyethane (1,1-DME), and mixtures of gBL with 1,2-DME and 1,1-DME.

Our observations indicated that lithium was most stable in gBL and mixtures of gBL with 1,2-DME, and much less stable in THF. Therefore, transport phenomena [9 - 11] were studied in the former solvents. Selected physicochemical properties of gBL, 1,2-DME and THF are given in Table 1 [7, 8].

The specific conductivity of LiClO_4 as a function of concentration is shown in Fig. 1(a). A much better electrical conductance of LiClO_4 solu-

TABLE 1

Selected physicochemical properties of gammabutyrolactone (gBL), 1,2-dimethoxyethane (1,2-DME) and tetrahydrofuran (THF)

Property	gBL	1,2-DME	THF
Formula	$\begin{array}{c} \text{H}_2 \\ \\ \text{H}_2\text{C}-\text{C} \\ \quad \diagup \\ \text{H}_2\text{C}-\text{O} \quad \text{C}=\text{O} \end{array}$	$\begin{array}{c} \text{H}_2\text{C}-\text{OCH}_3 \\ \\ \text{H}_2\text{C}-\text{OCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \diagup \\ \text{CH}_2-\text{CH}_2 \quad \text{O} \end{array}$
Molecular weight	86 091	90 123	72 108
Melting point (°C)	-43.5	-58	-108.5
Boiling point (°C)	204	83	64
Dielectric constant (25 °C)	39.1	7.2	7.39
Dipole moment (μD)	4.12	1.71	1.72
Density (25 °C) (g cm^{-3})	1.124	0.861	0.883
Viscosity (25 °C) (cP)	1.740	0.434	0.461
Donicity number			20
Specific conductance 25 °C ($\text{ohm}^{-1} \text{cm}^{-1}$)	2×10^{-8}	1×10^{-9}	4×10^{-9}

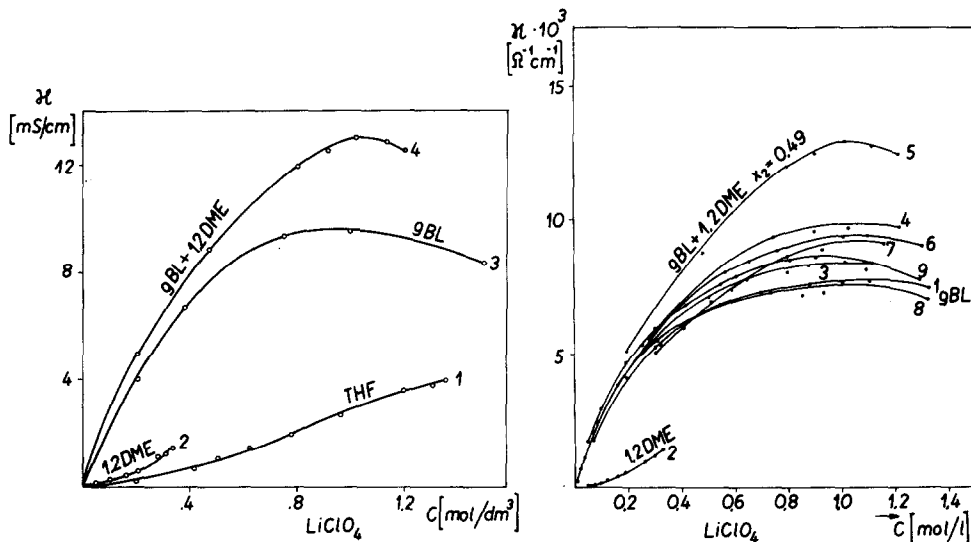


Fig. 1. (a) Specific conductivity, κ , at 25 °C as a function of LiClO_4 concentration in: 1, THF; 2, 1,2-DME; 3, gBL; 4, gBL + 1,2-DME (equimolar mixture). (b) Specific conductance, κ , at 25 °C vs. concentration, C , for LiClO_4 in: 1, gBL; 2, 1,2-DME; and in mixtures of gBL–1,2-DME for molar fraction 1,2-DME $x_2 = 0.1031$ (3); $x_2 = 0.3976$ (4); $x_2 = 0.4990$ (5); $x_2 = 0.5958$ (6); $x_2 = 0.6983$ (7); influence of H_2O added to gBL $x_2(\text{H}_2\text{O}) = 0.01$ (8), $x_2(\text{H}_2\text{O}) = 0.07$ (9).

tions in an equimolar mixture of gBL with 1,2-DME may be seen in curve 4 as compared with solutions of THF and 1,2-DME (curves 1 and 2). At the maximum on curve 4, which appears at a concentration of 1.1 mole/ dm^3 of LiClO_4 , the specific conductance, κ , is equal to $1.3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ (Fig. 1(b)).

Figure 2 shows the dynamic viscosity coefficient, η , of lithium perchlorate solutions in these solvents as a function of electrolyte concentration. η increases exponentially with concentration, and it can be seen that the viscosity for an equimolar mixture of gBL with 1,2-DME (curve 3) is not as high as for solutions of LiClO_4 in pure THF (curve 2).

Our cyclic voltammetric curves for the lithium electrode Li/Li^+ furnished some detailed information on the behaviour of lithium in 1M LiClO_4 solutions of organic solvents. An example is given in Fig. 3.

It will be seen that the current density is much higher in a solution of gBL with LiClO_4 than in THF with LiClO_4 .

The hysteresis of curve 1 is due to the presence of a passivation film which can be easily removed by anodic polarisation and then the lithium electrode can operate at high anodic current densities with relatively low overvoltages.

The sulfide cathodes were prepared in two ways. In the first case, commercial copper sulfide, CuS (Pfaltz und Bauer), was pressed into a brass die of the required dimension. In the second method, a mixture of sublimed sulfur and powdered electrolytic copper was pressed into the same die and

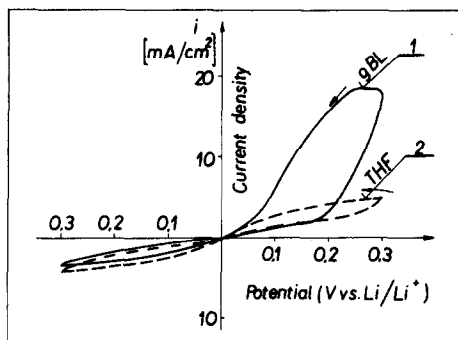
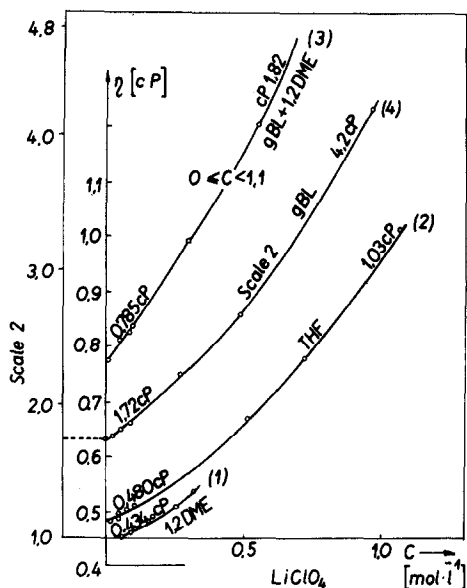


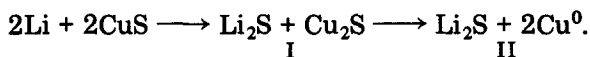
Fig. 2. Dynamic viscosity coefficient, η_{cp} , at 25 °C as a function of LiClO_4 concentration in: 1, 1,2-DME; 2, THF; 3, equimolar mixture of gBL + 1,2-DME; 4, gBL.

Fig. 3. Cyclic voltammetric sweeps for lithium anode in gBL with 1M LiClO_4 (1); in THF with 1M LiClO_4 (2). Sweep rate, 0.5 mV/s.

heated for an *in situ* synthesis [12]. The chemical composition of the cathode material after synthesis was determined by X-ray diffraction. Table 2 shows that at a temperature of 200 °C and a pressure of ca. 300 kg/cm² the dominant phase is CuS with a minimum admixture of Cu₂S.

3. Cell performances vs. cathode porosity

There are two reduction steps [3] and two fundamental products of the reaction of the Li/CuS system:



A high porosity of the CuS cathode material must be achieved because of the low solubility of Li_2S , which is one of the reaction products in the cathode area during operation of the cell. The correlation of porosity vs. pressing pressure is shown in Fig. 4. Curve 1 relates to the porosity of a mixture of copper and sulfur before synthesis *in situ*, curve 2 relates to the porosity of the cathode material after synthesis.

The pore size distribution was determined by two methods: the weight method and the mercury porosimetry method (Carlo Erba porosimeter). The specific surface of the cathode material was determined by the sorptometric method using Perkin-Elmer equipment.

TABLE 2

Chemical composition of cathode material CuS

Initial molar ratio: 1:1, total ageing time: 74 days, ●: dominating phase, +: minimal admixtures.

Pressing pressure (kg/cm ²)	Sintering temp. (°C)	Chemical components						Nonanalyzable impurities
		CuS	Cu ₂ S	CuO	Cu ₂ O	CuSO ₄	S	
300	170	● ●	+			+		+
300	200	● ●	+					+
300	230	● ●		+		+		+
600	170	● ●			+	+	+	
600	200	● ●	+	+	+			
600	230	● ●	+					+
1000	170	● ●	+	+	+	+	+	+
1000	200	● ●		+		+		+
1000	230	● ●	+					+

Figure 5 shows the distribution of pore sizes in a CuS electrode and their share of the total porosity. The predominant number of pore sizes has a radius within the range $4 - 6 \times 10^5 \text{ \AA}$.

Figure 6 shows the discharge characteristics of our first laboratory model lithium cells.

Curve 1 refers to the cell in which the cathode material was prepared by direct synthesis using the process parameters selected by our research team. Curve 2 concerns the cell in which the material was prepared from commercial CuS; this cell has much poorer characteristics.

These curves show the influence of porosity on the performance of the Li/CuS cells.

4. Miniature cells

Further intensive research on cells is being conducted, especially on different miniaturized versions. The most recent and smallest cell is shown in Fig. 7(a) and (b), which was developed jointly with the Cells and Batteries Central Laboratory in Poznań (CLAiO).

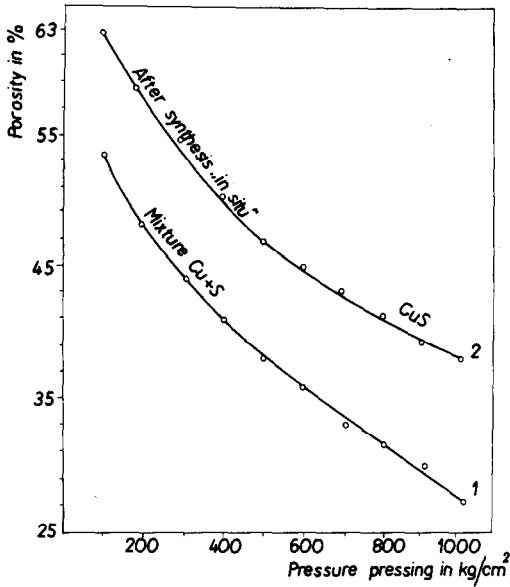


Fig. 4. Porosity vs. pressing pressure in kg/cm². Curve 1, Cu + S mixture before synthesis; curve 2, cathode material after synthesis *in situ*.

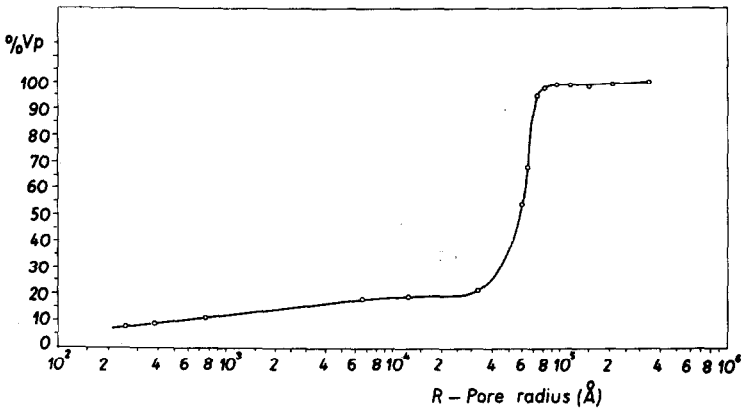


Fig. 5. Pore size distribution in cathode material; %V_p, volumetric percentage of porous material; R, pore radius (Å).

To date, six variants of the Li/CuS cell have been investigated — for two different cathode materials porosity values (40 and 50%) and for three different electrolyte solutions. Our best cells achieved a practical specific energy of ca. 300 W h/kg, a practical voltage of 2 and a capacity of about 95 mA h at 50% CuS porosity.

Figure 8 shows the discharge characteristics on a constant resistance load, $R_L = 100 \text{ k}\Omega$, during 250 days of continuous discharge.

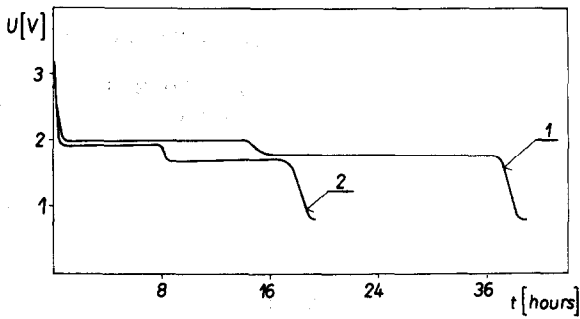


Fig. 6. Discharge characteristics of laboratory lithium cells: 1, CuS prepared by direct Cu and S synthesis; 2, CuS prepared from commercial CuS.

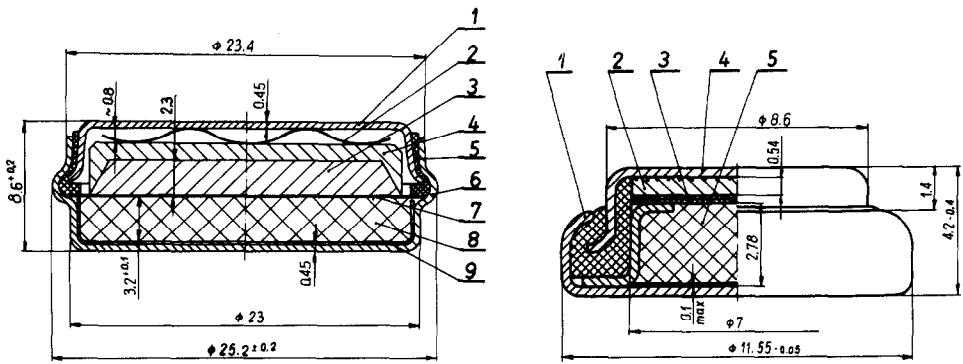


Fig. 7. (a) Miniaturized lithium cells with CuS cathode. 1, Lid; 2, spring; 3, lithium anode; 4, anode mould; 5, gasket; 6, casing; 7, separator; 8, cathode material CuS; 9, cathode mould. (b) A new version of the miniaturized Li/CuS cell.

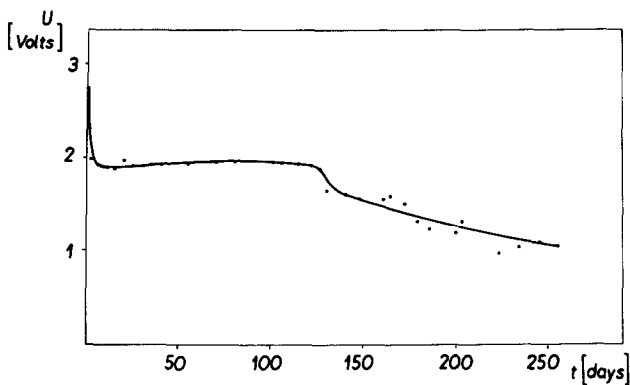


Fig. 8. Discharge characteristics on a constant resistance $R_L = 100 \text{ k}\Omega$.

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