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Ion-conductive macromolecular gels and membranes for solid lithium cells

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The formation of a quasi-solid gel electrolyte and its utilization in a lithium cell are described. The conditions of compatibility between constituents are defined as gelling of the system and absence of self-discharge. Also defined are the electrical, mechanical, and thermal properties required. Two types of electrolytes are considered:

(1) Ternary thermoplastic gels, principally based on polyvinyl acetals and polyacrylonitrile. Thin separators made of these materials generally require a porous or mesh support.

(2) Thermosetting self-supporting gels, obtained by cross-linking hydroxylated polyvinyl acetals or certain fluorinated polymers, which give the best compromise between mechanical properties, ionic conductivity, and solvent retention. Discharge tests made on single Li/CuS cells and on 10 V batteries indicate that these new solid elements show definite promise for applications which require high energy densities (1 kWh dm^{-3}) at low drains ($\ll$1 mA cm^{-2}).

List of abbreviations

DIAK	Dicinnamylidene hexanediamine
NMP	N-methylpyrrolidone
PAN	Polyacrylonitrile
PC	Propylene carbonate
PF_6	Hexafluoropropylene
PVAc	Polyvinyl acetate
PVB	Polyvinyl butyral
PVP	Polyvinylpyrrolidone
THF	Tetrahydrofuran
VF_2	Vinylidene fluoride

1. Introduction

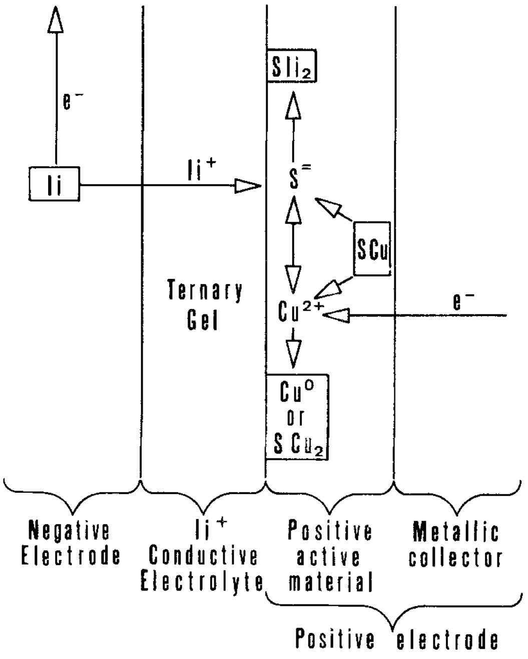

Fig. 1. Operation of a Li–CuS battery.

The continuing development of miniature electronic systems requires parallel improvements in energy sources, particularly with respect to energy density. Among the sources now commercially available, the mercury-zinc cell performs best, with an energy density of 400 Wh dm^{-3}. Development of higher-energy-density sources (700 Wh dm^{3}) involves using an alkali metal, such as lithium, as an anode. Lithium must be used in a totally anhydrous medium, since it reduces water. To be compatible with lithium, the non-aqueous electrolyte

Table 1. Criteria for compatibility between gel constituents

Type of interaction	*Problem posed*	*Proposed solution*	*Constituents selected*
Li – solvent	Li corrosion	Non-reduceable solvents	Propylene carbonate, etc.
Polymer-solvent	Gelling insufficient or absent	Systems with weak polymer-solvent interactions (see 4.1)	Polyvinyl acetals, polyacrylonitrile, polyfluoroalkenes
Li – polymer	Li corrosion	Non-reduceable compounds	The same
Salt – solvent	Voltage drop	Conductivity (solubility + dissociation)	Li or NH_4 perchlorates; $NaBF_4$, etc.
Salt – Li	Li corrosion	Non-reduceable ions	ClO_4^-, BF_4^-, etc.
	Li passivation during discharge	Cationic mobility	NH_4^+, Li^+, Na^+, etc.
Salt – polymer-solvent	Fluidification of the gel by lyotropic effect	Systems having weak ternary interactions	The same, except for Li^+
Positive material-solvent	Self-discharge by dissolution	Insoluble positive material	Sulphides: CuS, FeS_2, etc.
Electrolyte-atmosphere	Hydration followed by Li corrosion	Non-hygroscopic salt	NH_4ClO_4, $NaBF_4$, etc.
	Evaporation of solvent	Solvent with a low vapour pressure	Propylene carbonate
Electrolyte-reaction product (Li_2S)	Passivation owing to insolubility of discharge products	Reserve of solvent (gel) in the catholyte	The same

used must be chemically stable and must not dissolve the alkali metal (see Table 1).

A number of systems presently exist which use nonaqueous liquid electrolytes packaged in single cells; these produce 2–3·5 V. However, new applications, such as those in the microelectronic watch industry, require much higher voltages (10–15 V). For these a number of elements in series is necessary.

The electrolyte cannot be common to several elements because self-discharge currents will result. But the electrolyte of each element can be ‘immobilized’ by giving it a mechanically solid but elastic structure. The elastic property helps to absorb pressures applied during packaging, when the layers are stacked. The energy density is thus significantly increased (to 1 KWh dm^{-3}) because the single elements are placed directly in series in the same container.

This mechanically solid electrolyte acts as an ion-conductive layer for Li^+ ions passing between the lithium anode and a cathode material such as CuS (Fig. 1). This separator prevents direct contact between the lithium and copper sulfide layers, which would otherwise discharge spontaneously according to the reaction $2\,Li + CuS \rightarrow Cu + Li_2S$. The electrolyte must have adequate ionic conductivity and insolubility with respect to the positive active material (see below).

A process that reconciles these different conditions combines a non-aqueous salt solution with a polymer which forms a gel with respect to the solution. This polymer may be cross-linked to improve its mechanical and thermal properties. The mutual interactions of the three constituents – ions, solvent, polymer – determine the thermodynamic, mechanical, and electrical properties of the gel.

The development of batteries using such ionic gels therefore combines non-classicial macromolecular techniques with the fundamental electrochemical behaviour of batteries [1]. Because of limited contact between electrochemical technology and macromolecular chemistry, the combination is rarely seen in the literature. Applications in common aqueous batteries are generally empirical solutions of particular needs, using existing macromolecular materials which may not be optimum to the electrochemical requirements.

Dry-cell or ‘immobilized electrolyte’ batteries are the best example; gels of starch, carboxymethylcellulose [2], and polyacrylic or methacrylic acids [3] are used for zinc alkaline cells. Gelatin, polyethylene glycol, and polyvinyl alcohol are used in $Zn|ZnCl_2$ cells [2]. Colloidal inorganic gels of silica and alumina are used in lead-acid batteries [3]. Insoluble membranes which swell in aqueous media are also often used: cellophane [4], cellulose acetate [5], and ion exchangers [2, 5, 6] are used in zinc-silver batteries, where a certain ionic selectivity with respect to the zinc and silver ions is beneficial.

In non-aqueous media, macromolecular materials are rarely used, and immobilization of the electrolyte is not usually the objective. The principal reason for their use is their selectivity with respect to the soluble electro-active products coming from the electrodes: for example, ion-exchange membranes used in the Li | $LiClO_4$, butyrolactone | $CuCl_2$ cells [6, 7] prevent the migration of $CuCl_3^-$ ions into the negative compartment.

These existing structures do not provide either the absence of free liquid electrolyte or the compactness and mechanical and thermal properties necessary for assembly and miniaturization.

Up to the present, the study of gels has been considered a branch of macromolecular chemistry, without the participation of electrochemistry [8]. But macromolecular chemistry methods are very helpful in developing and optimizing new electrochemical components (synthesis and interaction studies of the gel constituents) [1].

2. Macromolecular gels as quasi-solid electrolytes

Initially we had envisaged a solid-electrolyte battery, such as Li | I or Li | AgI, but the high resistivity of the salt ($10^7\ \Omega$ cm), even in thin layers and doped with alkaline earth ions, proved to be insurmountable. An initial improvement was made by forming a solid solvate such as $LiI \cdot nCH_3OH$, by adding limited quantities of solvent. However, this process was abandoned because it was not reproducible.

We finally introduced a third, macromolecular component to form a reproducible ternary gel which also had satisfactory ionic conductivity ($\sim 10^3\ \Omega$ cm). We were able to develop a few satisfactory formulae with acceptable properties An early formula used methanol as a solvent with certain phenolic or vinylic polymers and lithium iodide; this gives good results which are, however, limited by a rather high resistivity, since the system must be desolvated before the cells are assembled because the lithium is attacked by the free solvent.

A more recent formula uses solvents compatible with lithium, such as propylene carbonate and butyrolactone, gelled by polyvinyl-formal. But addition of a lithium salt, the iodide or the perchlorate, produces an insufficiently rigid gel. The layer must be supported by a porous substance or framework. Strengthening the gel by cross-linking was found to be practical and useful. This provides support and increases the ionic conductivity, improving both the performance of the cell at high currents and its storage life.

3. Preparation of ternary gels

3.1. *Basic criteria for compatibility between the gel constituents and the environment*

Table 1 summarizes by type the interactions both among the constituents of the gel and between these constituents and their 'environment': lithium, the positive material or catholyte, reaction products such as Li_2S, and the external surroundings. The table indicates the types of problems encountered because of these interactions, and some proposed solutions. The constituents selected are the best known to date. The optimal choice at present is: ammonium perchlorate in propylene carbonate, with a polyvinylformal and polyvinylidene fluoride copolymer separator.

3.2. *Technological requirements*

Certain requirements are imposed by industrial conditions. Table 2 summarizes the solutions envisaged: cross-linking permits manipulation and high-temperature storage of the electrolytic gels during and after manufacture.

3.3. *Composition and modes of preparation*

Cross-linked gels are more difficult to prepare than thermoplastic gels, as shown in Table 3; nevertheless they combine a thin (0·1 mm) membrane with excellent retention of the electrolyte.

4. Fundamental study and optimization of the gels

After empirically developing a certain number of gels, we undertook a more fundamental study to establish chemical and physico-chemical bases for a more rational selection of the polymer.

Table 2. Technological requirements for the selection of gels

Desired property	*Proposed solution*
Thermal stability	1. Thermoplastic gels (PVF/PC or PAN/PC): raising the melting point by concentration of the polymer (20–40%).
Solvent retention (elimination of exudation)	2. Cross-linked gels ('thermo-setting'): cross-linking to suppress melting. Increase in polymer-solvent interactions. This factor is opposed to gelling.
Mechanical properties of gels:	
High rigidity coefficient	1. Thermoplastic gels: increase in the polymer concentration (20–40%). This decreases ionic conductivity.
High elastic limit and yield point	2. Cross-linked gels: No flow, and higher yield point.

Table 3. Composition and preparation of ternary gels

Category	*Composition*	*Preparation of electrolytes*
Thermoplastic gels	Polyvinylformal (PVF), Polyacrylonitrile (PAN) + PC + NH_4ClO_4 (sat.)	
(1) Soft	$\leqslant$ 10% for the polymer	Hot impregnation on porous support (asbestos)
(2) Hard	$\geqslant$ 20% for the polymer	Hot injection on insulating support (nylon)
Cross-linked gels (membranes)		
(1) Polyvinyl acetals	Polyvinylbutyral (PVB) (at 25% OH) cross-linked by epichlorhydrine or by titanium or silicon alkoxy-compounds in various solvents (THF, NMP, alcohols)	2 stages of preparation: formation of film and impregnation of the cross-linked membrane by PC + NH_4ClO_4 (sat.)
(2) Polyfluoroalkenes	Polyvinylidene fluoride (VF_2) or its copolymer with hexafluoropropylene (PF_6) cross-linked by Dicinnamylidene hexanediamine (DIAK) in methyl ethyl ketone	The same. 'Self-supported' membrane impregnated with PC + NH_4ClO_4 (sat.)

4.1. *Conditions of existence of the gels*

We measured the osmotic pressures of dilute solutions of the polymer and calculated the polymer-solvent interactions in terms of the second virial coefficient A_2 (8, 9, 10). We sought to correlate this interaction coefficient with the mechanical rigidity and the ionic conductivity of different gels of the same polymer. Results for different polymers in a dilute propylene carbonate solution are as follows:

Polymer	*Molecular weight*	A_2 *(g^{-2} ml · mole)*
Polyvinylformal (PVF)	36 000	0
Polyvinylpyrrolidone (PVP)	31 000	$3 \cdot 10^{-4}$
Polyvinyl acetate (PVAc)	43 000	$10 \cdot 10^{-4}$
Polyacrylonitrile (PAN)	41 000	$21 \cdot 10^{-4}$

Among these, only PVF and PAN can produce gels. It appears, therefore, difficult to establish a correlation between the A_2 parameter, which represents the intensity of the polymer-solvent interactions, and the ability to form a gel. These data agree with Bisschops' [11] observation that the gels of PAN with dimethylformamide form better than do those of PAN with dimethylacetamide, which however is a worse solvent.

Furthermore, when the gel PAN-sulfolane contains 20% by weight of the polymer rather than 30%, its position is reversed in relation to the other gels with regard to mechanical deformation (see Section 4.3). This indicates a substantial modification of the polymer-solvent interactions, as a function of the polymer concentration in the gel domain. This modification may also exist in the concentrated liquid, which could explain the lack of correlation between the value of A_2 in dilute solution and the rigidity of some gels. Such a correlation is indicated where the type and intensity of the polymer-solvent interactions change relatively little as the polymer solution is changed from dilute to concentrated and thence to a gel. In particular, for PVF, PVP, and PVAc, a clear correlation can be established between the reduction in polymer-solvent interactions (shown as a decrease in A_2) and the tendency to form gels.

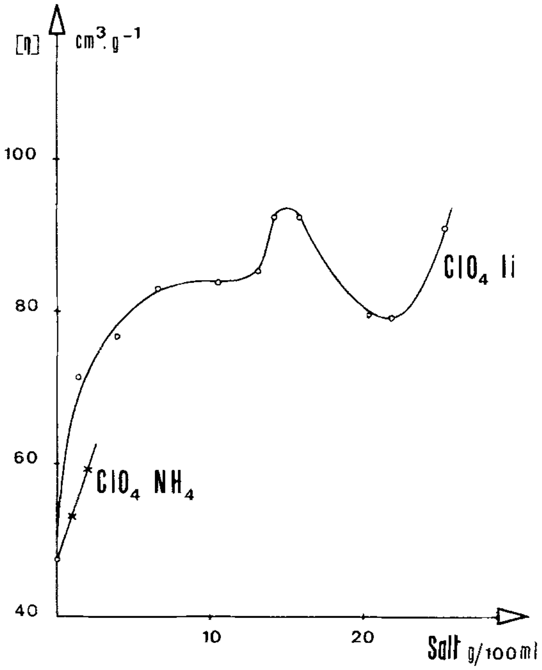

Fig. 2. Intrinsic viscosity of PVF in PC.

4.2. *Lyotropic effects of the conductive salt*

These effects appear principally as reductions of the rigidity of the gel and of its solvent-retaining capacity, as shown by the presence of an exudate. They are related to the swelling of macromolecular coils or aggregates [8] and, consequently, may be characterized by measuring the intrinsic viscosity (η) of dilute solutions of the polymer. In most cases, (η) increases as a function of the salt concentration (Fig. 2) and, simultaneously, the rigidity of the gels diminishes. The ions I^-, SCN^- and Li^+ display this effect most markedly and also greatly liquify the gels. The correlation between an increase in intrinsic viscosity in a dilute medium–resulting from the increase of polymer solvent 'contacts' – and a decrease in the rigidity of the gel is, however, subject to the same restrictions as is the correlation between the A_2 coefficient and the rigidity (Section 4.1.). So, $LiClO_4$ saturated PAN–PC gels are not more rigid than the corresponding PVF–PC gels even though, above a critical salt concentration, they possess a value of (η) lower than that of the pure gel (without salt).

The correlation of (η) with rigidity is nevertheless helpful, with reservations, in choosing a conductive salt which will least soften the gel. Thus, in accordance with the prediction of Fig. 2, NH_4ClO_4 was chosen in preference to $LiClO_4$.

4.3. *Mechanical properties*

The deformation characteristics of thermoplastic gels can also be used to select the gel best suited to industrial processes. In order of increasing rigidity and elastic resistance, we find

$$\text{PVF} - \text{PC} < \text{PAN} - \text{PC} < \text{PAN-sulfolane}$$

at three different concentrations (20, 30, and 40%), except for PAN-sulfolane at 20% polymer concentration, which is the least rigid and elastically resistant, Fig. 3.

4.4. *Electrical properties*

Values for resistivity of the gels were obtained from AC measurements at frequencies above 10 kHz, and from DC measurements based on the short-circuit currents of the Li|CuS cells.

These are in the range 2000–4000 Ω cm and agree well with each other. They depend very little on the nature of the polymer or on the electrolyte salt at saturation.

5. Applications to the manufacturing technology of lithium cells

5.1. *Preparation of test cells*

Each Li|CuS element is composed of a thin lithium anode, a gelled electrolyte fabricated by one of the techniques indicated in Table 3, and a catholyte or active positive material. This catholyte is CuS or some other semiconductive sulphide, such as pyrite, pyrrhotine or chalcopyrite, with a large capacity per unit volume. The powdered sulphide is held together with a 10% PVF gel in the proportion sulphide/gel = 70/30, and the mixture is

Table 4. Technical characteristics of Li | CuS cells (Capacity 20 mAh cm^{-2}; CuS/gel = 70/30)

Type of gel	*Composition*	*Open-circuit voltage* (V)	*Rate of discharge ensuring 100% efficiency* (μA cm^{-2})	*Is high-temperature storage possible?*	*Can elements be stacked in series?*
Thermoplastics					
(1) Soft	PVF/PC $\leqslant$ 10% + NH_4ClO_4 (sat.)	2·1–2·5	50–100	Elements having a liquid electrolyte	No
(2) Hard	PVF/PC $\geqslant$ 20% + NH_4ClO_4 (sat.)	2·1–2·5	$\leqslant$ 5	Yes, within limits. temperature < 50–60°C depending on hardness	No
Cross-linked gels	VF_2 + PF_6 impregnated with PC + NH_4ClO_4 (sat.)	2·1–2·5	# 50	Yes, at any temperature	Yes: fabrication of 10 V batteries realized

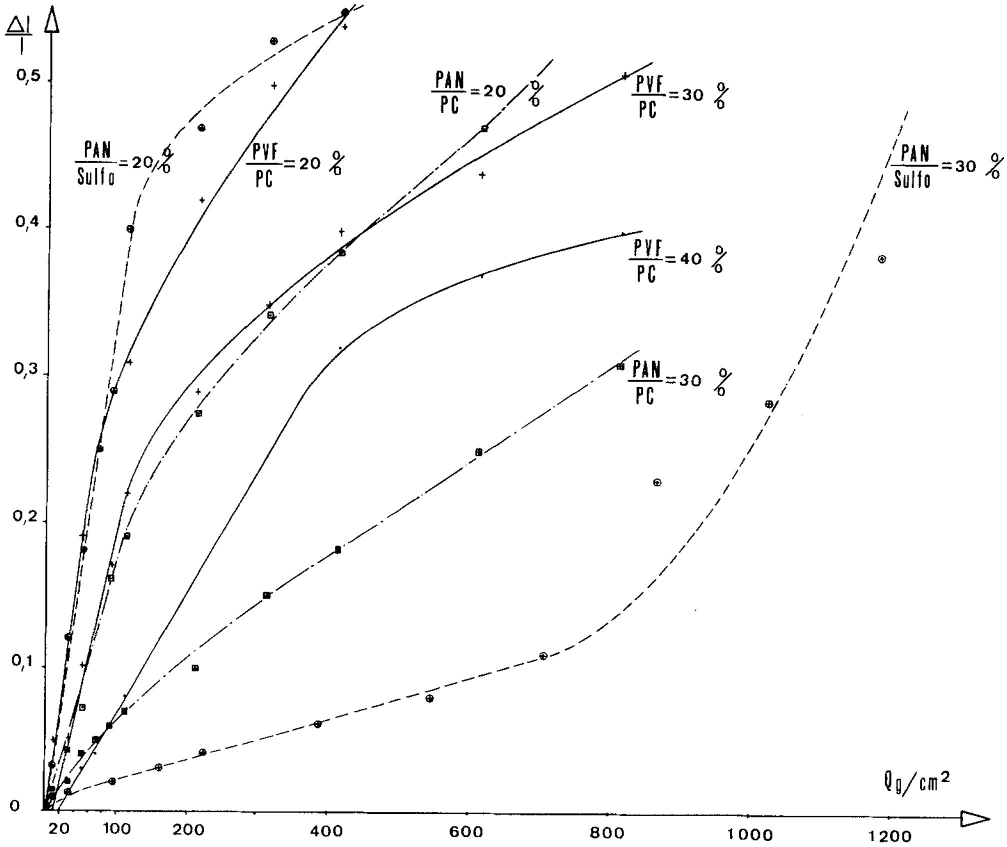

Fig. 3. Deformation curves $\frac{\Delta e}{e} = f(Q)$.

applied hot to a conductive mesh.

5.2. *Technical characteristics*

The principal characteristics of these cells are given in Table 4. The best over-all characteristics are displayed by the cross-linked gels, in particular those composed of a copolymer of vinylidene fluoride (VF_2) and hexafluoropropylene ($-PF_6-$)

swollen in a saturated solution of NH_4ClO_4. These gels possess good properties of electrical conductivity (~ 2000 Ω. cm), high rigidity and elastic limit, thermal infusibility of the cross-linked polymer, and solvent retention. The gels are well suited to commercial manufacturing technology, being easy to fabricate and manipulate, adaptable to stacking in series in a single-container cell, and relatively stable in storage even at warm ambient temperatures. They produce satisfactorily high energies per unit volume and high voltages at low currents.

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