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(54) Title: POLYMER ELECTROLYTE COMPOSITION

(57) **Abstract:** A composition for use as a polymer electrolyte, wherein said composition comprises one or more polar materials and one or more polyesters (polymers of carbonic acid); a process for preparing said composition; the use of said composition as a polymer electrolyte in coulometers, displays, smart windows, cells or batteries; and a cell and/or battery comprising said composition.

POLYMER ELECTROLYTE COMPOSITION

The present invention provides a composition for use
as a polymer electrolyte, a process for preparing said
composition, and its use, particularly in coulometers,
displays, smart window, cells and batteries.

5   Liquid electrolytes tend to suffer from problems
relating to the loss of electrolyte from the cell case
and require the use of cell seals. Under extreme
conditions, for example during short circuit abuse of
cells, the local heating within the cell case can lead to
10   seal rupture, even with the most sophisticated seal and
cell case design.

In general, solid electrolytes offer many
advantages over liquid electrolytes such as more
efficient use of space (no separator required), no risk
15   of electrolyte spillage, simplification of seal design
with resulting reduction of cost, extended temperature
range of cell operation, better cathode operation and
improved abuse resistance. Typical disadvantages of some
solid electrolytes are that they tend to have a
20   relatively low ionic conductivity and a poor mechanical
compatibility with certain types of electrode materials.

Such electrolytes may be used in coulometers, smart
windows or displays, cells and batteries.

During the last two decades a remarkable
25   international research effort has been dedicated to
studies in the domain of solvent-free solid polymer
electrolytes based on lithium salts. For example, such
research is discussed in Polymer Electrolyte Reviews – 1
and 2, J.R. MacCallum and C.A. Vincent (Elsevier, New
30   York, 1987 and 1989), Solid Polymer Electrolytes,
Fundamentals and Technological Applications, F.M. Gray

(VCH, New York, 1991), Applications of Electroactive
Polymers, B. Scrosati (Chapman and Hall, London, 1993),
Electrochemical Science and Technology of Polymers - 1
and 2, R.G. Linford (Elsevier, London, 1987 and 1991) and
5   Polymer Electrolytes, RSC Monographs, F.M. Gray (Royal
Society of Chemistry, London, 1997).

The motivation for this research has been provided
largely by the objective of developing novel lithium-
based primary and secondary cells.

10   Advantages of polymer electrolytes typically include
low processing costs, excellent mechanical properties,
the possibility of using a large area/thin film format,
variable cell configuration, low device weight, good
chemical stability, good thermal stability and access to
15   lithium chemistry.

However, whilst polymer electrolytes offer several
important advantages over conventional liquid non-aqueous
systems, the first generation of lithium ion conducting
solvent-free polymer electrolytes also suffered from
20   severe drawbacks.

Poly(ethylene oxide) (PEO) was the first polymer in
which salt solubilisation and ionic transport were
recognised.

D.E. Fenton, J.M. Parker and P.V. Wright reported the
25   preparation of crystalline complexes of sodium and
potassium salts with poly(ethylene oxide) in Polymer 14
(1973) 589.

P.V. Wright investigated the electrical
conductivities of various ionic complexes of
30   poly(ethylene oxide) in Br. Polymer J. 7 (1975) 319-327.

Poly(ethylene oxide) is still the most thoroughly
characterised electrolyte host matrix today. However, in
spite of the promise of initial results, systems based on
poly(ethylene oxide) were found to crystallise as salt-
35   polymer complexes or free polymer, resulting in a less

favourable conductivity behaviour in certain ranges of
salt concentrations and over a critical range of
operating temperatures.

During the years which followed the introduction of
the solid polymer electrolyte (essentially solvent-free
systems) a remarkable number of different polymer hosts
were studied, and, surprisingly it was soon widely
accepted that the most effective host polymer structure
was in fact the CH_2CH_2O group. Whilst the capacity of
this group to co-ordinate guest species is exceptional,
high molecular weight samples crystallise with a
significant reduction in the observed conductivity.

It has been found that ion conductivity is confined
to the amorphous domains of a polymer electrolyte and
that the tendency of the polymer electrolyte to
crystallise results in difficulties in the reproducible
preparation of electrolytes (G.G. Cameron, M.D. Ingram
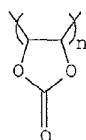and K. Sarmouk, Eur. Polym. J. 26 (1990) 1097-1101).

Various strategies have been applied to attenuate the
disadvantages of electrolytes based on the CH_2CH_2O
structural unit and electrolytes containing many
different salts, polymer architectures and plasticising
additive formulations have been reported and reviewed,
for example in Polymer Electrolytes, RSC Monographs, as
cited previously herein.

Recently, a new strategy has been proposed by T.
Yamamoto, M. Inami and T. Kanbara in Chem. Mater. 6
(1994) 44-50, and by X. Wei and D.F. Shriver in Chem.
Mater. 10 (1998) 2307-2308, based on the use of
relatively rigid polymer hosts with comparatively high
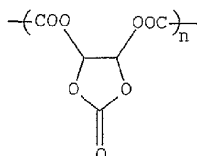values of glass transition temperature, Tg.

Yamamoto et al. describe the preparation and
properties of polymer solid electrolytes based on
poly(vinyl alcohol) (PVA) and poly[arylene(1,3-

4

imidazolidene-2,4,5-trione-1,3-diyl)] (poly(parabamic acid), PPA).

Wei et al. describe two rigid polymer systems of poly(vinylene carbonate) (PVIC) (I) and poly(1,3-dioxolan-2-one-4,5-diyl oxalate) (PVICOX) (II) for the preparation of polymer electrolytes. The systems are said to display both favourable conductivity and mechanical properties.

(I)   (II)

The conductivities of the PVICOX system (II) are shown to be about 2-4 orders of magnitude higher than those of the PVIC system (I).

Wei et al. hypothesise that this is due to the irregularity of the PVICOX system (II) which frustrates close packing, thereby increasing static free volume and conductivity.

The developments of Yamamoto et al. and Wei et al. seem to go against the accepted precepts of polymer electrolyte operation. However, surprisingly high conductivities have been reported.

Although many other polymer architectures have been assessed as host polymers, prior to the publication of the results reported by Yamamoto et al., the ethylene oxide unit was widely believed to be the best option for high ionic conductivity as a consequence of its unique combination of structural and thermodynamic factors.

The results obtained by Yamamoto et al. and Wei et al. confirm that even polymers which do not contain the ethylene oxide structural unit may be effective media for

the dissolution and efficient transport of charged
species.

It has been shown in the art that the introduction of
small polar molecules into the polymer network often
results in a marked improvement in the observed ionic
conductivity of the polymer.

Cameron et al., as previously cited herein, noted a
decrease in viscosity and an increase in conductivity
when 10 wt. % of the plasticisers tetrahydrofuran (THF)
or propylene carbonate (PC) were added to
poly(tetrahydrofuran) (PTHF) and to a copolymer of
ethylene oxide and propylene oxide (50:50 by weight).

R. Huq, R. Koksbang, P.E. Tonder and G.C. Farrington
reported the results of a study on the effect of a mixed
plasticiser on the conductivities and the
physical/chemical properties of radiation-polymerised
polyether electrolytes. The mixed plasticiser
compositions of ethylene carbonate and propylene
carbonate containing 1M lithium hexafluoroarsenate (V)
($LiAsF_6$) were found to possess better thermal, mechanical
and lithium cycling properties.

M.S. Michael, M.M.E. Jacob, S.R.S. Probaharan and S.
Radhakrishna reported in Solid State Ionics 98 (1997)
167-174 that a novel class of esters of benzene-1,2-
dicarboxylic acids such as dioctyl phthalate (DOP),
dibutyl phthalate (DBP) and dimethyl phthalate (DMP) had
been used as plasticisers in high molecular weight PEO-
lithium perchlorate matrix to improve the room
temperature ionic conductivity of polymer-salt complex.

Although this improvement in conductivity in certain
electrolyte systems has been interpreted in terms of an
alteration in the transport mechanism (F. Croce, S.D.
Brown, S.G. Greenbaum, S.M. Slane and M. Salomon, Chem.
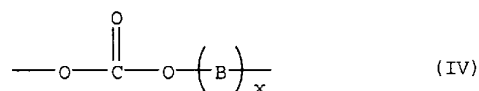Mater. 5 (1993) 1268-1272) or plasticisation of the

polymer structure (Cameron et al. as cited previously herein), other effects may also contribute.

There has now been found a novel class of polymer electrolytes which are based on polymers that possess good
5   ionic conductivity and excellent mechanical properties.

The present invention is based on a composition that can be used as a polymer electrolyte, which composition comprises one or more polar materials and one or more polyesters of formula III,

$$\left[A \right]_y \qquad (III)$$

10

wherein y is from 1.5 to 80 and each unit A may be identical or different and is of the structure IV,

$$ -O-\overset{\overset{\displaystyle O}{\|}}{C}-O-\left(B \right)_x \qquad (IV)$$

wherein X is from 1 to 5 and each unit B may be identical or
15   different and is of the structure V,

$$ -\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R^1}{|}}{C}}- \qquad (V)$$

wherein R and R^1 are each, independently, hydrogen, an optionally substituted hydrocarbyl group or an inert functional group.

20   In one aspect, the present invention provides a composition for use as a polymer electrolyte, wherein said composition comprises one or more polar materials and one or more polyesters of carbonic acid and a polyhydric alcohol selected from 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol,
25   1,5-pentanediol, 1,6-hexanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, trimethylolethane, glycerine and pentaerythritol, wherein the or each said polyester has a

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weight average molecular weight greater than 30000.

In a further aspect, the present invention provides a process for preparing a composition for use as a polymer electrolyte in accordance with the invention, wherein a solution comprising a homogeneous mixture of the polyester and the polar material are prepared in a solvent. Optionally, the solvent of said solution can be allowed to evaporate under an inert atmosphere.

By "polar materials" in the present invention is meant salts and proton conductor systems. Typical proton conductor systems include phosphoric acid and sulphamide.

By "hydrocarbyl group" in the present invention is meant a group containing only carbon and hydrogen. Unless otherwise states, the number of carbon atoms is

preferably from 1 to 4. Examples of hydrocarbyl groups include methyl, ethyl and propyl.

In the present invention, the phrase "optionally substituted hydrocarbyl" is used to describe hydrocarbyl groups optionally containing one or more "inert" heteroatom-containing functional groups. By "inert" is meant that the functional groups do not interfere to any substantial degree with the ionic conductivity and/or mechanical properties of the resulting composition. Said inert groups may include ethers and polyethers. Such inert groups may act as plasticisers. Non-limiting examples of such inert groups are $-CH_2CH_2OCH_3$ and

$-CH_2CH_2OCH_2CH_2OCH_3$.

Inert functional group: a group other than optionally substituted hydrocarbyl which is inert under the process conditions. By "inert" is meant that the functional group does not interfere to any substantial degree with the ionic conductivity and/or mechanical properties of the resulting composition.

Compositions according to the present invention generally comprise polyesters having a weight average molecular weight, M_w, greater than 30,000, preferably greater than 75,000, and more preferably greater than 250,000.

The weight average molecular weight, M_w, of the polyester may be determined by several techniques which give closely similar results. M_w may be easily determined by gel permeation chromatography (GPC) with calibration of the polyester as will be appreciated by those skilled in the art. Alternatively, M_w may be determined by light scattering, as described in ASTM D 4001-93.

Said polyesters generally have a glass transition temperature, Tg, in the range of from -60 to 20 °C, preferably in the range of from -50 to 10 °C, and more preferably in the range of from -30 to 5 °C.

Polyesters according to the present invention are generally polymers of carbonic acid made by the condensation polymerisation of one or more different polyhydridic alcohols with phosgen or derivatives thereof. Said polyesters may also be formed by the ring opening polymerisation of a cyclic carbonate as described previously in the art or by transesterification with dialkylcarbonate or alkylene carbonate.

Polyhydric alcohols used in the preparation of said polyesters are selected from 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, trimethylolethane, glycerine and pentaerythritol.

The preferred polyesters in respect of the present invention are poly (trimethylene carbonate) and esters of other polyhydric alcohols described above.

The amount of polyester incorporated in the composition is generally in the range of from 50 to 99 wt. %, preferably in the range of from 60 to 94 wt. %, and more preferably in the range of from 65 to 83 wt. % based on the composition.

The amount of polar material incorporated in the composition is generally in the range of from 50 to 1 wt. %, preferably in the range of from 40 to 6 wt. %, and more preferably in the range of from 35 to 17 wt. % based on the composition.

The composition of the present invention may comprise salts such as quaternary ammonium salts, for example ammonium thiocyanate, and/or metal salts.

Metal salts that may be generally employed in the composition of the present invention include those wherein the metal is selected from lithium, sodium, potassium, nickel, zinc, silver and lanthanides such as neodymium, europium, erbium and thulium.

In particular, triflate, perchlorate, bromide, chloride, iodide, bis(trifluoromethylsulphonyl)imide, tetrafluoroborate, trifluoromethanesulphonate, hexafluoroarsenate (V), thiocyanate, acetate, dichlorosulphonimide, fluorochlorosulphonimide, sulphonate and tetrachloroaluminate salts of the above-mentioned metals are preferred.

According to the present invention, preferred metal salts are lithium metal salts.

Particularly preferred lithium metal salts are lithium triflate, lithium perchlorate, lithium bromide, lithium chloride, lithium iodide, lithium bis(trifluoromethylsulphonyl) imide, lithium tetrafluoroborate, lithium trifluoromethanesulphonate, lithium hexafluoroarsenate (V), lithium thiocyanate, lithium acetate, lithium dichlorosulphonimide, lithium fluorochlorosulphonimide, lithium sulphonate and lithium tetrachloroaluminate.

Compositions may be prepared with a range of salt concentrations by adding different quantities of the salt to the composition. The composition of the resulting mixture may be identified by indicating the value of n. In this context, n is the molar ratio of monomer units per mole of added salt. Generally, n is in the range of from 1 to 100, preferably in the range of from 1 to 80, more preferably in the range of from 1 to 15 and most preferably in the range of from 1 to 5.

In a preferred embodiment of the present invention, the composition is a solid, that is to say, the polymer electrolyte is a solid, solvent-free polymer electrolyte.

However, in another aspect of the present invention, the composition may further comprise a solvent. Thus, the polyester may act as an immobiliser to a non-aqueous electrolyte of a salt in a solvent, for example, lithium tetrafluoroborate, lithium perchlorate, lithium hexafluoroarsenate, lithium tetrachloroaluminate and /or lithium bromide in acetonitrile, propylene carbonate, dimethylsulphoxide (DMSO), etc.

The composition according to the present invention may further comprise one or more plasticiser compounds.

Said plasticiser compounds may be typically selected from propylene carbonate, ethylene carbonate, dimethylsulphoxide, dioctyl phthlate, dibutyl phthalate, diethyl phthalate, dimethyl phthalate, butyrolactone, dimethyl carbonate, diethyl carbonate, bis(2-ethylhexyl) sebacate and/or trimethylene carbonate.

Plasticisers may be typically used at doping levels in the range of from 1 to 50 wt. %, preferably in the range of from 1 to 20 wt. % and more preferably in the range of from 5 to 15 wt. %.

Compositions according to the present invention may be prepared by weighing out polyester and salt components and adding a volume of solvent to produce a solution comprising a homogeneous mixture of the components. Said solution may be quite viscous in character.

In a preferred embodiment of the present invention, the solvent of said solution may be allowed to evaporate under an inert atmosphere. Such a procedure typically allows the formation of a thin flexible film of the composition.

Solvents that may be typically used in the formation of compositions according to the present include dry tetrahydrofuran, dry acetonitrile, dry methanol and dry ethanol.

The inert atmosphere that is typically employed in the formation of compositions according to the present invention may include dry argon, dry nitrogen, or dry helium.

5   In another embodiment of the present invention, the composition may be prepared by polymerising polyester monomers *in situ* in the presence of the salt.

Compositions according to the present invention may be used as polymer electrolytes in coulometers, displays,

10   smart windows, cells and batteries. The present invention therefore also provides a cell and/or battery comprising said composition.

By "smart window" is meant a variable transmission device wherein the transmission of light through the

15   device may be controlled electrochemically, darkening a thin anode or cathode on the inner surface of the glass layer of the window.

The present invention will now be illustrated by the following Examples, which should not be regarded as

20   limiting the scope of the present invention in any way, by reference to the accompanying drawings, in which:-

Figure 1 shows the variation of conductivity with reciprocal temperature for polymer electrolytes based on a (TMC)n lithium triflate system;

25   Figure 2 shows the variation of conductivity with reciprocal temperature for polymer electrolytes based on a (TMC)n lithium perchlorate system;

Figure 3 shows conductivity isotherms for polymer electrolytes based on a (TMC)n lithium triflate system;

30   Figure 4 shows conductivity isotherms for polymer electrolytes based on a (TMC)n lithium perchlorate system;

Figure 5 shows the effect of bis(2-ethylhexyl) sebacate upon the conductivity of a (TMC)$_9$ lithium

35   triflate system;

Figure 6 shows the effect of diethyl phthalate upon the conductivity of a $(TMC)_9$ lithium triflate system;

Figure 7 shows the effect of trimethylene carbonate upon the conductivity of a $(TMC)_9$ lithium triflate system;

Figure 8 shows thermogravimetric analysis of pure p(TMC) and polymer electrolytes based on a $(TMC)n$ lithium perchlorate system and a $(TMC)n$ lithium triflate system;

Figure 9 shows a comparison of temperatures of onset of weight loss of electrolytes based on lithium perchlorate and lithium triflate;

Figure 10 shows thermal analysis of polymer electrolytes based on a $(TMC)n$ lithium triflate system; and

Figure 11 shows thermal analysis of polymer electrolytes based on a $(TMC)n$ lithium perchlorate system.

Experimental Section

1. Materials

Poly(trimethylene carbonate) (p(TMC)) with a molecular weight of 3.2×10^5 was prepared by catalysed bulk polymerisation and characterised by gel permeation chromatography (GPC). The polymer was a very flexible elastomer and was dried before use at 65 °C, under vacuum, for a period of about 7 days.

Lithium triflate (95 %, ex. Aldrich) and lithium perchlorate (99.99 %, ex. Aldrich) were dried under vacuum at 180 and 150 °C respectively, for 7 days and then stored in a high integrity, dry argon-filled glovebox.

All subsequent sample preparations, manipulations of salt and measurements were carried out under a dry argon atmosphere.

Unless otherwise stated, solvent grades employed
herein were purchased ex. Aldrich and were anhydrous,
purity 99.9 %, inhibitor free and packaged under argon.

2. Sample Preparation

5   Homogeneous solutions of p(TMC) and lithium triflate
or lithium perchlorate in tetrahydrofuran (THF) were
prepared by adding known weights of p(TMC) and the
appropriate lithium salt to a convenient volume of
solvent and stirring the components within a dry argon-
10   filled preparative glovebox.

The resulting solutions were cast into glass rings on
glass plates and the solvent was then removed slowly by
locating the moulds in an isolated chamber within the
preparative glovebox. The atmosphere of the chamber was
15   re-circulated through a column of molecular sieves to
effect a slow evaporation and to form films of about 150
μm thickness. These films were dried at 65 °C under
vacuum for 3 days to remove residual solvent.

3. Measurements

20   Total ionic conductivities of electrolyte samples
were determined using a constant volume support with gold
blocking electrodes located within a Buchi TO 150 oven.

The sample was measured with a type K thermocouple
placed close to the electrolyte film and impedance
25   measurements were carried out with a Solartron 1250
Frequency Response Analyser and 1286 Electrochemical
Interface, between 25 and 100 °C. Measurements of
conductivity were effected during heating cycles and at
temperature intervals of about 7 °C. The reproducibility
30   of conductivities obtained in initial and subsequent
heating cycles was extremely good and taken as
confirmation of the efficiency of the support operation
and mechanical stability of the samples.

Polymer electrolyte film sections were subjected to
35   thermal analysis under a flowing argon atmosphere between

-40 and 350 °C and at a heating rate of 5 deg.min^{-1} using
a Mettler TC11 controller and a DSC 20 oven. Samples in
the form of disks were cut from polymer films and
presented for analysis in 40 µl aluminium cans with
5   perforated lids.

Samples for thermogravimetric studies were also
prepared by cutting sections of suitable dimensions from
electrolyte films. These sections were transferred to
open platinum crucibles and analysed using a Rheometric
10   Scientific thermobalance operating under an argon
atmosphere. A heating rate of 5 deg.min^{-1} was used to
analyse all the electrolyte samples.

4. Results and Discussion

(i) Ionic Conductivity

15   The total ionic conductivity of electrolytes with a
range of composition, based on lithium perchlorate and
lithium triflate were studied.

The results of conductivity measurements on various
compositions within a series of electrolyte films with
20   compositions of lithium triflate and lithium perchlorate
with values of n from 2 to 73 are illustrated in Figures
1 and 2, respectively.

Over the entire range of compositions, and in both
systems, the variation of conductivity with reciprocal
25   temperature was found to be linear within experimental
error with no breaks or inflections. The highest
conductivity in the lithium triflate-based electrolyte
system was recorded at a composition with n close to 9.
In contrast, the conductivity of electrolytes based on
30   lithium perchlorate electrolytes continued to increase
with concentration up to values of n of 2.

The activation energy of the ion transport through
the polymer medium, assuming linear behaviour, was
approximately 40 kJ.mol^{-1}, with a variation of less than

7 % over the composition range studied, suggesting that the properties of the polymer host determine the ion transport, not the nature of the guest salt species.

The effect of guest salt concentration on total ionic conductivity can be clearly seen in Figures 3 and 4.

These results show the substantial variation of total ionic conductivity with the concentration of the guest salt species (lithium triflate or lithium perchlorate) is greater than that found with "conventional" electrolytes based on solvent-free PEO-based systems such as those described by D. Fauteux, Ph.D. Thesis, University of Quebec, 1986 and in the Proceedings of the 2nd International Symposium on Solid Polymer Electrolytes (B. Scrosati (Ed.), Elsevier, Amsterdam, 1990, p. 235).

In the lithium triflate-based electrolyte, the gradual increase in the conductivity with the salt concentration and the number of charge carriers available suddenly alters at about n=20. From this composition to n=9, the conductivity rises to a maximum and then falls rapidly in electrolytes with greater salt content. This sudden decrease in conductivity is fairly common in solvent-free polymer electrolyte systems and is normally explained in terms of an increase in the number of polymer-salt interactions resulting in restrictions in the mobility of the polymer chain segments which is responsible for ion transport.

Although the density of charge distribution over triflate and perchlorate anions is similar, the total ionic conductivity observed in the art with lithium perchlorate-based polymer electrolytes is generally greater than that of those containing triflate ions at a similar concentration.

This behaviour is also apparent in the p(TMC)-based systems studied herein. No phase separation was observed in electrolytes doped with lithium perchlorate, even at

compositions close to n=2, in contrast to the triflate-
based electrolytes which reach a solubility limit at
about n=5. At close to n=2, the lithium perchlorate-
containing electrolyte showed a maximum conductivity of

5   approximately 3 x 10^{-4} $\Omega^{-1}cm^{-1}$.

       As may be confirmed by reference to Figure 4, the
total ionic conductivity of lithium perchlorate-based
p(TMC) electrolytes continues to increase with salt
concentrations to very high compositions of added salt.

10   The p(TMC) polymer, as an amorphous, polar
macromolecular host, is a more suitable solvent for the
preparation of polymer electrolytes than PEO. Even
without additives, the electrolytes display encouraging
levels of performance which may be further improved with

15   the use of suitable free-volume enhancing components.
       Studies have shown significant improvement in the
total ionic conductivity of the p(TMC) as a result of the
use of even fairly low quantities of plasticiser.
       A series of electrolytes based on a constant lithium

20   triflate concentration was prepared with the inclusion of
a plasticiser molecule in the casting solution.
       Plasticisers bis(2-ethylhexyl) sebacate, diethyl
phthalate and trimethylene carbonate were used at doping
levels of between 5 and 15 wt. %. As expected, the

25   presence of plasticiser increased the ionic conductivity
(Figures 5 to 7). However, at doping levels of greater
than about 15 wt. %, the mechanical properties began to
degrade and the material became gel-like.
       Trimethylene carbonate was found to be an efficient

30   conductivity enhancer without decreasing the mechanical
robustness of the electrolyte film.
       (ii) Thermal Analysis
       The results of thermal analysis of samples of polymer
electrolyte according to the present invention are

35   illustrated in Figures 8 to 11.

Studies of the thermal behaviour of electrolytes
based on both lithium perchlorate and lithium triflate
showed a glass transition at about -18 °C which was
almost unaffected by the salt content between n of 85 and
5   about 15.

As the salt content is further increased to values of
n less than about 15, a slight shift of Tg to higher
temperatures is perceptible.

This suggests that significant interaction between
10   the guest ionic species and the polymer host chains only
takes place at these higher concentrations of lithium
salt. No fusion of polymer-salt complexes or uncomplexed
polymer is apparent in any of the electrolytes studied
and no other thermal events are observed until
15   temperatures of about 200 °C when an endothermic peak
likely to be due to polymer decarboxylation is
registered.

The results of thermogravimetric studies are
consistent with this interpretation and the thermograms
20   of pure polymer, and electrolytes containing high
concentrations of lithium perchlorate or lithium triflate
are illustrated in Figure 8.

In accordance with results previously observed with
PEO-based electrolytes (Proceedings of the 2nd
25   International Symposium on Solid Polymer (B. Scrosati
(Ed.), Elsevier, Amsterdam, 1990, p. 49)), the onset of
the degradation process is dependent upon electrolyte
composition, confirming that the salt has a destabilising
influence upon polymer host.

30   As can be seen from Figure 9, the pure host polymer
p(TMC) began to degrade thermally at a temperature close
to 230 °C. Polymer electrolytes with values of n between
85 and 2 were found to be less thermally stable than the
pure polymer. Electrolytes with high concentrations of
35   lithium perchlorate were found to degrade at about 160 °C

while lithium triflate-based materials were stable to
approximately 180 °C. These thermal stabilities are
considered to be adequate for applications of the
electrolytes in cells or batteries operating at low or
5   moderate temperatures.

As this effect of guest ionic species has been
interpreted as a consequence of the interaction between
the guest ions and the polymeric solvent, weakening the
bonds within the macromolecular backbone, this
10   observation also suggests that the interaction between
the guest salt and the host polymer increases with the
salt content.

Lithium perchlorate-containing electrolytes show
thermal behaviour which is similar to that observed with
15   lithium triflate-based films at low temperatures, but
with a completely different degradation thermogram. As
may be confirmed by reference to Figures 10 and 11, while
the onset of the perchlorate degradation is similar to
the process observed with the triflate, once initiated,
20   the electrolyte samples suffer a strongly exothermic
process, the intensity of which is dependent on the
amount of salt present in the sample.

The electrolytes formed with high lithium salt
compositions (up to n=2) for lithium perchlorate-based
25   material were obtained as transparent, flexible films.
These materials have mechanical properties which are
suitable for application in primary or secondary cells or
batteries which suffer from anode or cathode expansion
during cell discharge or re-charge. The polymer
30   electrolyte, being mechanically flexible will adapt to
such changes in electrode dimension, maintaining ionic
contact with the electrode material.

In conclusion, a new host polymer matrix based on
polyester rather than polyether coordinating units, with

lithium triflate and lithium perchlorate guest species,
has been used to form solvent-free electrolytes.

The highest ionic conductivity observed with these
new electrolytes at a salt-rich composition, is similar
5   or better than that observed in many other solvent and
additive-free systems.

The results of thermal analysis have confirmed that
polymer electrolytes based on this host matrix are
completely amorphous. All electrolyte samples showed
10   adequate windows of thermal stability for practical
devices.

Throughout this specification and the claims
which follow, unless the context requires otherwise,
the word "comprise", and variations such as
15   "comprises" and "comprising", will be understood to
imply the inclusion of a stated integer or step or
group of integers or steps but not the exclusion of
any other integer or step or group of integers or
steps.
20   The reference to any prior art in this
specification is not, and should not be taken as, an
acknowledgment or any form of suggestion that that
prior art forms part of the common general knowledge
in Australia.
25

11 Feb 2005

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A composition for use as a polymer electrolyte, wherein said composition comprises one or more polar materials and one or more polyesters of carbonic acid and a polyhydric alcohol selected from 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, trimethylolethane, glycerine and pentaerythritol, wherein the or each said polyester has a weight average molecular weight greater than 30000.

2. A composition according to Claim 1, wherein the polyester is poly(trimethylene carbonate).

3. A composition according to Claim 1 or 2, wherein the polar material is a lithium metal salt.

4. A composition according to any one of Claims 1 to 3, wherein said composition is a solid.

5. A composition according to any one of Claims 1 to 4, wherein said composition further comprises one or more plasticiser compounds.

6. A composition for use as a polymer electrolyte substantially as hereinbefore described with reference to the Examples.

7. A process for preparing a composition according to Claim 1, wherein a solution comprising a homogeneous mixture of the polyester and the polar material are prepared in a solvent.

8. The process according to Claim 7, wherein the solvent of said solution is allowed to evaporate under an inert

11 Feb 2005

2001283972

atmosphere.

9. A process according to Claim 7 or 8, wherein the polar material is a salt.

10. Use of a composition according to any one of Claims 1 to 6 as a polymer electrolyte in a coulometer, display, smart window, cell or battery.

11. A cell and/or battery comprising a composition according to any one of Claims 1 to 6.

12. A process for preparing a composition according to Claim 1 substantially as hereinbefore described with reference to the Examples.

DATED this 10th day of February, 2005
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
By DAVIES COLLISON CAVE
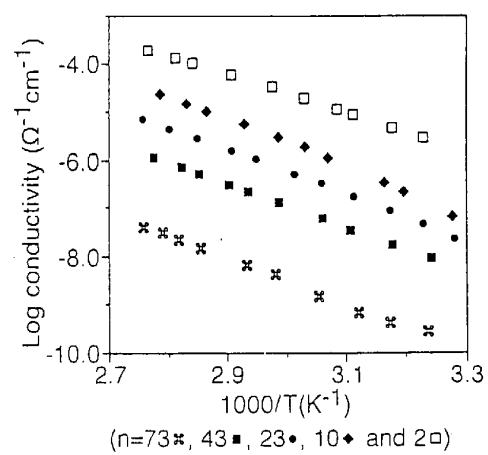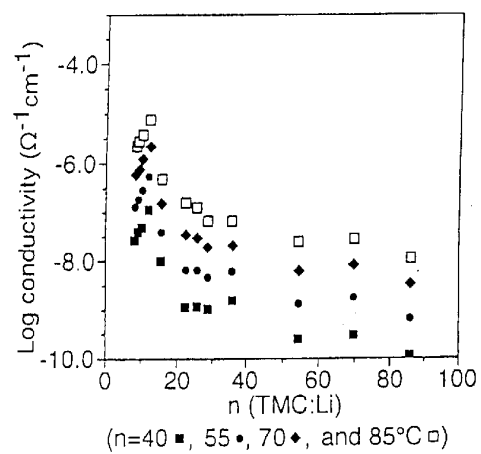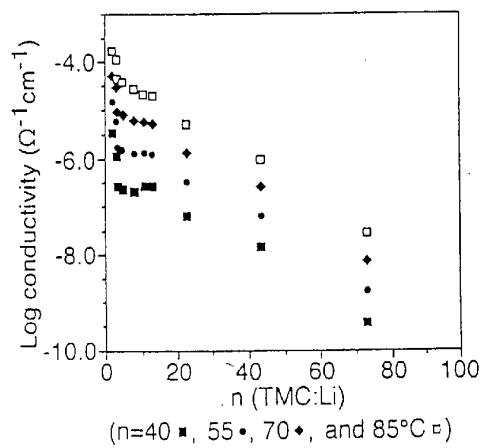Patent Attorneys for the Applicants

Fig.1.

$(n=55 \blacksquare, 35 \bullet, 10 \blacklozenge, 9 \square \text{ and } 7 \circ)$

Fig.2.

$(n=73 \text{✻}, 43 \blacksquare, 23 \bullet, 10 \blacklozenge \text{ and } 2 \square)$

Fig.3.

(n=40 ■, 55 ●, 70 ♦, and 85°C □)

Fig.4.

(n=40 ■, 55 ●, 70 ♦, and 85°C □)

Fig.5.

((a) 0%, (b) 5.3%, (c) 14.7%)

Fig.6.

((a) 0%, (b) 10%)

Fig.7.

((a) 0%, (b) 10%)

Fig.8.

(a) $(TMC)_8 LiClO_4$, (b) $(TMC)_{10}LiCF_3SO_3$ and (c) pure p (TMC)

Fig.9.

Temperature of onset of weight loss/°C

240

pure
polymer

220

65

45

200

43.4

70

35

lithium
perchlorate

180

22.6

25

10

lithium
triflate

12.8

8

160

Electrolyte composition

Fig.10.

n=6
n=15
n=20
n=35
n=70
n=85

1.0 W/g
exo →

100   200   300
Temperature/°C

Fig.11.

n=5
n=8
n=11
n=13
n=23
n=43

2 W/g
exo →

100   200   300
Temperature/°C