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(54) ORGANIC SOLVENT ELECTROLYTES FOR HIGH SPECIFIC ENERGY PRIMARY CELLS

(71) We, SOCIETE ANONYME DITE: SAFT—SOCIETE DES ACCUMULATEURS FIXES ET DE TRACTION, a French Body Corporate of 156, avenue de Metz 93230 Romainville, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electrolytes containing aprotic organic solvents for use in high specific energy primary cells and in particular for lithium cells. Such electrolytes comprise one or several aprotic organic solvents which are compatible with lithium and a solute which is an alkaline salt and may be lithium perchlorate, lithium hexafluoroarsenate, lithium hexafluorophosphate, lithium tetrafluoroborate, etc. It has already been noticed that electrolytes having a solvent which is constituted by a mixture of two organic substances, preferably a cyclic ether and an ester or a cyclic ether and a linear ether, have higher conductivities than electrolytes having a solvent which is constituted by a single organic substance at the same concentration of solvent. (See French patents 1,579,466, 2,054,736 and 2,176,568; respective U.S. equivalents: 3,511,716, 3,701,688 and 3,960,595; respective British equivalents: 1,208,934, 1,260,632 and 1,412,174. This mixture has made it possible to use ethylene carbonate which is solid at ordinary temperatures as a solvent. Nonetheless, it can happen that the mixture of two solvents gives only an additive effect without increasing the conductivity (as the case of mixtures of tetrahydrofuran and dioxolane for example), or even that the conductivity is lower than that which would have been calculated knowing the proportions of the solvents and the conductivities of the pure solvents. For example, ether oxyde has this effect with tetrahydrofuran, or acetic anhydride with dioxolane. The choice of

solvents for composing the mixture is thus important and difficult to predict *a priori*.

The conductivity of electrolytes having several solvents whose mixture gives an increase in conductivity, can be further improved by means of the present invention.

It provides an electrolyte for lithium primary cells, comprising a mixture of a plurality of aprotic organic solvents which are compatible with lithium and a solute which is alkaline salt, wherein the organic solvents are three in number, of which the first is chosen from the category of solvents having a dielectric constant equal to or greater than 35, the second from the category of linear polyethers whose ether functional groups are in the γ position, and the third from the category of solvents having a high solvation power dissolving large quantities of an alkaline salt, the solvents of the three categories being such that the conductivity maxima of the electrolytes obtained by mixing the solvents in pairs are higher than the conductivity maxima of the electrolytes obtained from each of the solvents, and each of the said solvents being in a volume proportion lying between 20% and 60%.

It has been observed that molar solutions of an alkaline salt such as lithium perchlorate prepared from such ternary mixtures have conductivities which are higher than those of solutions obtained by mixing pairs of each of the three solvents constituting the mixture. It has also been observed that the conductivity maxima of these binary solutions are lower than the maximum of the ternary solution.

With the proportions of each solvent lying between 20 and 60% by volume, depending on the solvents used, the highest conductivities are obtained, but generally the conductivity maxima of these solutions do not vary much with proportion in this range.

Amongst the possible first solvents,

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propylene carbonate and ethylene carbonate are preferred.

Amongst the possible second solvents there is the dimethylether group with 1-2 dimethoxyethane as the first choice, but also including dimethylether of diethylene glycol and dimethylether of triethylene glycol.

1-3 dioxolane is advantageously used as the third solvent.

The invention will be better understood with the help of the following examples illustrated in the accompanying drawings in which:

Figure 1 is a graph showing as a function of solute concentration the conductivity curves of a ternary electrolyte in accordance with the invention and of several binary electrolytes obtained from the solvents of the ternary electrolyte as well as the conductivities of electrolytes obtained from the solvents alone;

Figure 2 is a graph analogous to that of Figure 1 showing the conductivity curves of two ternary electrolytes according to the present invention, the conductivity curves of the corresponding binary electrolytes, and the conductivity curves of the corresponding single solvent electrolytes;

Figure 3 shows the conductivity curves of two electrolytes in accordance with the invention as a function of temperature $T(^{\circ}\text{C})$ as well as those of the corresponding binary electrolytes and single solvent electrolytes;

Figure 4 shows the discharge curves $V=f(t)$ of electric cells comprising the electrolytes in accordance with the invention as well as the corresponding binary electrolytes and the corresponding single solvent electrolytes; and

Figure 5 shows the discharge curves $V=f(t)$ of two electric cells in accordance with the invention operating under different conditions to those of Figure 4.

The first examples concern the conductivity of ternary electrolytes in accordance with the invention, in comparison with the conductivity of the electrolytes obtained from each of the solvents of the ternary electrolytes used on their own and with the same solvents mixed in pairs (binary electrolytes). The solute in all these electrolytes is lithium perchlorate. In Figure 1 the X-axis shows the concentration in moles per litre of lithium perchlorate and the Y-axis shows the conductivity of the electrolytes in $10^{-3}\Omega^{-1}\text{cm}^{-1}$.

For curve A the solvent is propylene carbonate (PC) which has a dielectric constant of 64. For curve B the solvent is dimethylether of diethylene glycol (DMDG) which is a linear polyether whose ether functional groups are in the γ

position. For the curve C the solvent is dioxolane (DO) which is a cyclic ether having a high solvation power.

The curve AB shows the conductivities of binary electrolytes whose solvent is an equal volume mixture of PC and DMDG. It can be seen that it is above the curves A and B. The curve AC shows the conductivities of binary electrolytes whose solvent is an equal volume mixture of PC and DO. Its conductivity maximum is situated above those of the curves A and C. The curve BC shows the conductivities of binary electrolytes whose solvent is an equal volume mixture of DMDG and DO. Its maximum is also situated above the maxima of B and C.

The curve ABC corresponds to ternary electrolytes in accordance with the invention where the solvent is an equal volume mixture of PC, DMDG and DO. It can be seen that it is above the curves AB, AC and BC.

Analogous curves were obtained by replacing the DMDG by dimethyl ether of triethylene glycol (DMTG). In this case it should be pointed out that the ternary mixture PCDMTG-DO with volume proportion of 1-0.5-1 gave a conductivity of $11 \times 10^{-3}\Omega^{-1}\text{cm}^{-1}$ for a 1 M solution of LiClO_4 , near to that of the electrolyte in accordance with the invention of the curve ABC.

In the same manner Figure 2 shows the conductivities of two other examples of electrolytes in accordance with the invention and the corresponding single solvent electrolytes and the corresponding binary solvent electrolytes.

In this figure the curve A again shows the conductivities of electrolytes whose solvent is PC and the curve C the conductivities of electrolytes whose solvent is DO and likewise the curve AC electrolytes whose solvent is an equal volume mixture of PC and DO. The curve D shows the conductivities of electrolytes whose solvent is 1-2 dimethoxyethane (DME) which a linear polyether whose ether functional groups are in the γ position.

The curve AD shows the conductivities of binary electrolytes whose solvent is an equal volume mixture of PC and DME. It is noticeably higher than the curves A and D. The curve DC shows the conductivities of electrolytes whose solvent is an equal volume mixture of DME and DO, and it is situated above the curves D and C.

Finally the curve ADC shows the conductivities of ternary electrolytes in accordance with the invention whose solvent is an equal volume mixture of PC, DME and DO. It can be seen that not only is its maximum situated above those of the curves AC, AD and DC, but also that it is

situated further to the left than the highest maximum of these curves, i.e. that it is obtained for a lesser concentration of lithium perchlorate which is advantageous since it is an expensive substance.

The curves in dashed lines on this figure show the conductivities of electrolytes where the propylene carbonate has been replaced with ethylene carbonate (EtC). The conductivities of a single solvent electrolyte corresponding to EtC has not been shown since this material is solid at ambient temperatures. In contrast, the curve EC shows the conductivities of electrolytes whose solvent is an equal volume mixture of EtC and DO, the curve ED, the conductivities of electrolytes whose solvent is an equal volume mixture of EtC and DME. The maxima of these curves are well above those of the curves D and C.

The curve EDC shows the conductivities of ternary electrolytes in accordance with the invention where the solvent is constituted by an equal volume mixture of EtC, DME and DO. It has its maximum situated above the curves EC, ED and DC.

It can be seen in all these examples that the conductivities of electrolytes in accordance with the invention are higher than those of the corresponding binary electrolytes known in the prior art, at least for lithium perchlorate in concentrations below 2 M.

These curves are given for equal volume mixtures of the solvents, but similar results have been obtained by taking, for example, mixtures of 25% PC, 50% DME and 25% DO with a conductivity maximum of $14.5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, i.e. even higher than the conductivity maximum for equal volumes. (The percentages are volume percentages). The same is true for mixtures where EtC replaces PC since the conductivity maximum of the 25-50-25 mixture is again slightly higher than that of the equal volume mixture.

Likewise analogous results have also been obtained by replacing the lithium perchlorate with lithium hexafluoroarsenate giving conductivity maxima which are even higher since the equal volume mixtures of PC, DME and DO gave a maximum of $17 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for a 1.10 molar concentration and the equal volume mixtures of EtC, DME and DO gave a maximum of $17.5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for the same concentration. In contrast, tests performed with lithium trifluoromethane sulfonate gave a maxima which were noticeably lower since they were situated around $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, but ternary electrolytes in accordance with the invention continued to have a net

advantage over the binary or single solvent electrolytes.

Figure 3 shows the temperature variations of the conductivity of the electrolytes where the solute is lithium perchlorate at a concentration of 1 M. Conductivity is shown along the Y-axis in units of $10^{-3} \Omega^{-1} \text{cm}^{-1}$ and temperature along the X-axis in degrees centigrade.

The curve A3 corresponds to an electrolyte whose solvent is PC and the curve C3 to an electrolyte whose solvent is DO. The curves DC3, AC3 and AD3 correspond to binary electrolytes where the solvent is constituted by equal volume mixtures of DME-DO, PC-DO and PC-DME respectively. The binary electrolytes as a whole give higher conductivities than those of the single solvent electrolytes. The curves ADC3 and EDC3 represent the conductivities of two electrolytes in accordance with the invention where the solvents are constituted by equal volume mixtures of PC-DME-DO and EtC-DME-DO respectively. It can be seen straight away that the conductivities of the electrolytes in accordance with the invention which are already higher at ordinary temperatures, remain higher down to extremely low temperatures.

Figure 4 relates to the discharging of cells which were all assembled in the same way and differ only in their electrolyte solvent. They are cylindrical cells of 13.7 mm diameter and 22.9 mm height. The cathode, adjacent to the can, is annular and is constituted by a mixture of cupric oxide CuO with 7% graphite in such a quantity that its theoretical capacity is 1.3 Ah. The lithium anode, of tubular form, has an initial area beside the separator of 3.3 cm^2 . The separator is a felt of glass fibres. The electrolytes are 1.25 M solutions of lithium perchlorate. The cells were discharged through a resistance of 30 ohms which corresponds to an average current density of about 9 mA/cm^2 . The curves show the discharge time in hours along the X-axis and the tension V in volts along the Y-axis.

In Figure 4 the curve F corresponds to the discharge of a cell where the electrolyte solvent is pure dioxolane (DO). The curve G shows the discharge of a cell where the electrolyte solvent is an equal volume mixture of propylene carbonate (PC) and dioxolane, and the curve H the discharge of a cell where the electrolyte solvent is an equal volume mixture of propylene carbonate and 1-2 dimethoxyethane. These cells are discharged for longer than the single solvent cell. The curve K corresponds to the discharge of a cell containing a ternary electrolyte in accordance with the invention whose solvent has the following composition (by

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volume) PC=60%, DME=20%, and DO=20%. For the curve I the electrolyte solvent is composed of the same substances but mixed in equal volumes. The curve J is given by a cell where the electrolyte solvent has the following composition: PC=20%, DME=20% and DO=60%. The curve of a cell where the electrolyte solvent is a mixture of PC=20%, DME=60% and DO=20% has not been shown but it is situated, practically to the end, in-between I and J. Taking the end voltage as 0.75 volts, the discharge efficiencies are 44.6% for I, 44.7% for J and 39.7% for the cell with the last mentioned electrolyte. It can be seen, particularly with the curves I and J, that the cells in accordance with the invention give better results than the cells including single solvent electrolytes (15.4% efficiency) or binary solvent electrolytes (21% and 34% respectively). It should be noticed that discharging through a 30 ohms resistance represents extremely harsh discharge conditions and that the tensions and discharge capacities are low under such conditions. By replacing the lithium perchlorate in the electrolytes in accordance with the invention with 1 M lithium hexafluoroarsenate in the equal volume mixture of EtC-DMEDO a discharge curve comparable with the curve I was obtained under the same conditions (52.6% efficiency).

Cells analogous to those which were used for making Figure 4 were prepared by replacing the cupric oxide with ferrous disulfide FeS₂. With electrolytes in accordance with the invention and in particular with equal volume PC-DME-DO electrolytes in which 1.25 M lithium perchlorate has been dissolved, these cells give discharge curves which are little different from that which was obtained using cupric oxide. Figure 5 shows the discharge curves of such cells through a 120 ohm resistance (curve M) in comparison with the discharge curve of cupric oxide cells through the same resistance (curve L). It can be seen that while the discharge capacity of the iron bisulphide cells is a little lower than that of the cupric oxide cells, its voltage level is in contrast slightly higher. The electrolytes in accordance with the invention are thus quite usable with cells using ferrous disulphide positive electrodes.

Without going beyond the scope of the invention any element could be replaced by an equivalent element.

WHAT WE CLAIM IS:-

1. An electrolyte for lithium primary cell comprising a mixture of aprotic solvent which are compatible with lithium and a solute which is alkaline salt, wherein the organic solvents are three in number of which the first is chosen from the category of solvents having a dielectric constant equal to or greater than 35, the second from the category of linear polyethers whose ether functional groups are in the γ position, and the third from the category of solvents having a high solvation power dissolving large quantities of an alkaline salt, the solvents of the three categories being such that the conductivity maxima of the electrolytes obtained by mixing the solvents in pairs are higher than the conductivity maxima of the electrolytes obtained from each of the solvents, and each of the said solvents being in a volume proportion lying between 20% and 60%.

2. An electrolyte according to Claim 1, wherein the first solvent is chosen from the group of esters, propylene carbonate and ethylene carbonate.

3. An electrolyte according to Claim 1 or 2, wherein the second solvent is 1-2 dimethoxyethane, dimethyl ether of diethylene glycol, or dimethyl ether of triethylene glycol.

4. An electrolyte according to any preceding claim, wherein the third solvent is 1-3 dioxolane.

5. An electrolyte according to any preceding claim, wherein the solute is chosen from the group: lithium perchlorate, lithium hexafluoroarsenate and lithium trifluoromethane sulfonate.

6. A three-solvent electrolyte substantially as herein described with reference to any of the three-solvent examples whose properties are shown in the graphs of Figures 1, 2 and 3 of the accompanying drawings.

7. A high specific energy electrochemical primary cell comprising a lithium negative electrode, a positive electrode and an electrolyte which is an electrolyte according to any preceding claim.

8. A cell according to Claim 7, wherein the active material of the positive electrode is cupric oxide.

9. A cell according to Claim 7, wherein the active material of the positive electrode is ferrous disulphide.

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