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[54] **ELECTROLYTE FOR USE IN AN ALL INORGANIC RECHARGEABLE CELL AND LITHIUM INORGANIC CELL CONTAINING THE IMPROVED ELECTROLYTE**

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252/62.2

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[57] ABSTRACT

An improved electrolyte is provided in a lithium/sulfur dioxide rechargeable cell, the electrolyte comprising a solution of a stable, highly conductive liquid electrolyte complex $\text{LiAlCl}_4\text{—}3\text{SO}_2$ and up to about 50 percent by weight of sulfuric chloride as a cosolvent.

10 Claims, No Drawings

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ELECTROLYTE FOR USE IN AN ALL INORGANIC RECHARGEABLE CELL AND LITHIUM INORGANIC CELL CONTAINING THE IMPROVED ELECTROLYTE

The invention described herein may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

This invention relates in general to an improved electrolyte for use in all inorganic rechargeable cell and to an all inorganic rechargeable cell including the improved electrolyte and in particular to an improved electrolyte for use in a lithium/SO₂ rechargeable cell and to a lithium/SO₂ rechargeable cell including the improved electrolyte.

BACKGROUND OF THE INVENTION

An all inorganic Li/SO₂ rechargeable cell generally includes a lithium anode, a porous carbon cathode and a stable highly conductive liquid electrolyte complex LiAlCl₄-xSO₂. This complex is rapidly formed when the commonly used LiAlCl₄ electrolyte salt reacts with SO₂ gas or SO₂ liquid. Although the initially formed liquid complex has the formula LiAlCl₄-3SO₂, additional lowered LiAlCl₄ salt concentration can be achieved at will by diluting the above electrolyte with additional SO₂. Thus, electrolyte with formulas LiAlCl₄-xSO₂ where x is at least 3 can be prepared. The starting electrolyte LiAlCl₄-3SO₂ has a very high specific conductivity of 0.1 S/cm. The fact that this is the highest known conductivity for any ambient temperature non aqueous electrolyte makes this general class of electrolytes extremely valuable.

One difficulty with the use of this electrolyte is however, that during cell discharge, the insoluble reduction product is deposited in the porous carbon cathode. Simultaneously, some of the LiAlCl₄ electrolyte salt is also precipitated in the porous carbon cathode. The coprecipitation of electrolyte salt is partially responsible for the severely reduced capacity currently plaguing this system.

SUMMARY OF THE INVENTION

The general object of this invention is to provide an improved lithium inorganic rechargeable cell system. A more particular object is to minimize or even eliminate LiAlCl₄ coprecipitation and thus improve cell capacity.

It has been found that the aforementioned objects can be attained by adding a suitable cosolvent to the electrolyte to allow excess LiAlCl₄ that would normally precipitate to dissolve. The requirements of an effective cosolvent are:

(A) The cosolvent should be capable of rapidly dissolving the LiAlCl₄ salt and, in order to minimize IR losses, must in the process form a reasonably conducting electrolyte solution.

(B) The cosolvent should be extremely miscible with liquid SO₂.

(C) The cosolvent must not become easily oxidized during cell charging which typically takes place at 4.0 volts relative to lithium.

(D) The cosolvent should not become chemically degraded in the presence of AlCl₃ or chlorine, both of which are formed during cell charging.

A particularly effective cosolvent has been found to be sulfonyl chloride, SO₂Cl₂. One would not expect that

the addition of SO₂Cl₂ as a cosolvent would be able to improve cell capacity in Li/SO₂ rechargeable cells since the specific conductivity of pure SO₂Cl₂ is very poor. That is, pure SO₂Cl₂ is one million times less conductive than is the LiAlCl₄-3SO₂ electrolyte.

Experimental results were obtained in small laboratory cells. The cells include a lithium anode, a porous carbon cathode made from high surface area carbon black and a LiAlCl₄ electrolyte salt.

The following electrolytes were tested: (1) LiAlCl₄-3SO₂; (2) LiAlCl₄-3SO₂+10% SO₂Cl₂; (3) LiAlCl₄-3SO₂+20% SO₂Cl₂; and (4) LiAlCl₄-SO₂Cl₂.

The results of these experiments are shown in the following Table:

ELECTROLYTE	FIRST CYCLE	TENTH CYCLE
	CAPACITY mA·H	CAPACITY mA·H
LiAlCl ₄ -3SO ₂	9	14
LiAlCl ₄ -3SO ₂ + 10% SO ₂ Cl ₂	32	20
LiAlCl ₄ -3SO ₂ + 20% SO ₂ Cl ₂	52	18
LiAlCl ₄ -SO ₂ Cl ₂	20	0

The results clearly show that Li/LiAlCl₄-3SO₂ cells constructed with 10% and 20% added SO₂Cl₂ had longer capacities than either Li/LiAlCl₄-3SO₂ cells or even Li/LiAlCl₄-SO₂Cl₂ cells. It is clear that on the TENTH CYCLE, the advantage of the addition of low percentages of SO₂Cl₂ is evident. Cells containing more than 50% added SO₂Cl₂ could not be cycled ten times.

We wish it to be understood that we do not desire to be limited to the exact details as described for obvious modifications will occur to a person skilled in the art.

What is claimed is:

1. An improved electrolyte for use in an all inorganic rechargeable cell, said electrolyte comprising a solution of a stable, highly conductive liquid electrolyte complex LiAlCl₄-xSO₂ where x is at least 3, and up to about 50 percent by weight of a cosolvent that is: (a) capable of rapidly dissolving a LiAlCl₄ salt and in the process forming a reasonably conducting electrolyte solution; (b) extremely miscible with liquid SO₂; (c) not easily oxidized during cell charging; and (d) not chemically degraded in the presence of reaction products formed during cell charging.

2. An improved electrolyte according to claim 1 wherein the cosolvent is sulfonyl chloride.

3. An improved electrolyte for use in a lithium/sulfur dioxide rechargeable cell, said electrolyte comprising a solution of a stable, highly conductive liquid electrolyte complex LiAlCl₄-xSO₂, where x is at least 3, and up to about 50 percent by weight of a cosolvent that is:

(a) capable of rapidly dissolving LiAlCl₄ salt and in the process forming a reasonably conducting electrolyte solution;

(b) extremely miscible with liquid SO₂; (c) not easily oxidized during cell charging which takes place at about 4.0 volts relative to lithium; and (d) not chemically degraded in the presence of AlCl₃ or Cl₂, both of which are formed during cell charging.

4. An improved electrolyte according to claim 3 wherein the liquid complex has the formula LiAlCl₄-3SO₂.

5. An improved electrolyte according to claim 4 wherein the cosolvent is from about 10 percent to about

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20 percent by weight of the electrolyte of sulfuryl chloride.

6. An improved electrolyte according to claim 3 wherein the cosolvent is sulfuryl chloride.

7. A lithium inorganic rechargeable electrochemical cell comprising lithium as the anode, a porous carbon as the cathode, and a solution of a stable, highly conductive liquid electrolyte complex $LiAlCl_4-xSO_2$ where x is at least 3, and up to about 50 percent by weight of a cosolvent that is: (A) capable of readily dissolving $LiAlCl_4$ salt and in the process forming a reasonably conducting electrolyte solution; (B) extremely miscible with liquid SO_2 ; (C) not easily oxidized during cell charging which takes place at about 4.0 volts relative to

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lithium; and (D) not chemically degraded in the presence of $AlCl_3$ or Cl_2 , both of which are formed during cell charging; as the electrolyte.

8. A lithium inorganic rechargeable electrochemical cell according to claim 7 wherein the liquid complex has the formula $LiAlCl-3SO_2$.

9. A lithium inorganic rechargeable electrochemical cell according to claim 8 wherein the cosolvent is from about 10 percent to about 20 percent by weight of the electrolyte of sulfuryl chloride.

10. A lithium inorganic rechargeable electrochemical cell according to claim 7 wherein the cosolvent is sulfuryl chloride.

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