

carbonate (i.e., propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, butyl carbonate, etc.), acyclic carbonate or other organic mixture. The other organic mixture are DME, DMF, DMSO, γ -butyrolactone, N-methyl pyrrolidone, ester, lactone, and low molecular weight ether, etc. The metallic salts dissolved in nonaqueous electrolytes function as ionic conductivities medium are: LiBF_4 , LiClO_4 , LiPF_6 , LiSbF_6 , LiI , LiBr , LiCl , LiAlCl_4 , LiSCN , LiAsF_6 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$, $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_3\text{C}$, etc., further including conductive salt compounds. The concentration of the electrolytes mentioned above is generally 0.2-0.3M.

[0048] The manufacturing process of this present invention is simple, and is suitable for industrial processes. There are two different ways to produce as following: 1) the procedure of one step, that is by adding nonaqueous electrolyte solution, which is monomer solvent, during polymerizing reaction; or 2) the procedure of two steps, that is by, first, preparing crosslinked polymer membranes and nonaqueous electrolyte solution respectively, and second, then soaking the crosslinked polymer membranes in the nonaqueous electrolyte solution for absorbing.

[0049] To make sure the stability of batteries, the electrolytes, materials for making batteries, which are either liquid or gel phase must possess widely range of operation voltage. This present invention, for instance of gel-type crosslinked PAN electrolytes, its liquid electrolyte concentration is substantially equal to 1M and the decomposition potential values of different liquid electrolytes containing lithium salts are completely above 5V (vs. Li/Li^+), in arrangement is $\text{LiPF}_6 > \text{LiBF}_4 > \text{LiCF}_3\text{SO}_3 > \text{LiClO}_4$. Those results indicate that this present invention is potential to the lithium polymer secondary batteries.

[0050] In conclusion, this present invention can overcome all disadvantages of prior-art.

[0051] A primary object of the present invention is to provide a composite gel-type polymer electrolyte membrane, as the secondary battery's separator between the positive and the negative electrodes, and that possesses the advantages of high ionic conductivities, superior mechanical strength, simply manufacturing process, and well compatible to electrodes.

[0052] To achieve the object mentioned above, the crosslinked composite gel-type polymer electrolyte membrane consists of gel-type PAN electrolytes, PVdF polymers and liquid electrolytes. The gel-type PAN electrolytes are copolymerized by acrylonitrile (AN) monomers and crosslinked monomers with two terminal acrylic acid ester function groups. The PVdF polymers mean that PVdF polymers whose molecule weight is over 5000, or contain over 80% PVdF-co-HFP polymer. The liquid electrolytes are made from using nonaqueous solvent (i.e., cyclic carbonate, acyclic carbonate, amide solvent, lactone solvent, ether solvent, etc.) to dissolve alkaline or alkaline earth metallic salts. The content of liquid electrolytes is 10%~200% of polymers of electrolyte membranes. The conductivity of the crosslinked composite gel-type polymer electrolyte membrane is above 1×10^{-4} S/cm. Moreover, the composite polymer electrolyte membranes can be added below 20% of PEO, soften chain polymers, or in organically porous fillers to enhance its mechanical strength.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0053] The AN and crosslinked monomer reagents, used in the following preferred embodiments, have already removed the stabilizer by standard purification process.

EXAMPLE 1

Preparation of Crosslinked Polyacrylonitrile Polymer Membranes (Excluding Electrolytes)

[0054] Add 0.5 g of PEO into the mix of 4 g of DMF, 6 g of AN monomers and 2 g of TGD, stir at the temperature under 50° C. for 6 hours until that to be the uniform solution, and then put it at room temperature. After dissolving 0.1 g of benzoyl peroxide in 3 g of AN and became transparent solution, mix with the prior mixture, and then stir slowly until those as uniform gel solution. Finally, mold the uniform gel solution by the gap size of 150-250 μm , thermal polymerize by heating temperature of 60° C. for 12 h with cover, and then will obtain dry membrane of crosslinked polyacrylonitrile polymer in 150-250 μm thickness.

EXAMPLE 2

Preparation of Crosslinked Polyacrylonitrile Polymer Membranes (Including Electrolytes)

[0055] Weigh 1.5 g of PEO and dissolve in 20 g of 1M $\text{LiClO}_4/\text{EC/PC}$ solution, stir and heat to reach the temperature of 100° C., and then cool at room temperature when became uniform solution. Add 0.15 g of BPO in the mix of 3.5 g of An and 1 g of TGD, stir sufficiently at room temperature, and mix with prior mixture. After stirring at room temperature and mixture became semi-transparent, mold the semi-transparent mixture by the gap size of 150-250 μm , thermal polymerize by heating temperature of 60° C. for 12 h with cover, and then will obtain crosslinked polyacrylonitrile polymer membranes in 150-250 μm thickness.

EXAMPLE 3

Preparation of Crosslinked Composite PVdF-PAN Gel-Type Polymer Electrolyte Membranes

[0056] The manufacturing process of gel electrolyte solution including AN monomer is similar to the procedure described in example 2.

[0057] Weigh 3 g of PVdF and dissolve in 10 g of acetone, stir and heat to reach the temperature of 50° C., and then cool at room temperature after dissolving completely. Mix that with different amount of gel electrolyte solution, stir at room temperature until solution became uniform gel solution, and then form the gel solution into thin membrane by drawknife (400 μm) onto the mold plate. Remove large amount of acetone in the dryer box, which is full of N_2 gas, for 12 h, will obtain semi-transparent membrane, and then thermal polymerize by heating temperature of 60° C. for 12 h with glass cover. After reaction completely, we can obtain the crosslinked composite gel-type polymer electrolyte membranes, PVdF, in the size of 150-250 μm .

EXAMPLE 4

The Thermogravimetric Analysis (TGA) Experiment of Crosslinked PAN Electrolyte Membranes and Uncrosslinked PAN Powders

[0058] Thermal stability analysis of crosslinked PAN electrolyte membranes, in the example 1, and uncrosslinked