

SINGLE ION CONDUCTOR CROSS-LINKED POLYMERIC NETWORKS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. provisional application Ser. No. 60/294,954, filed May 31, 2001 and U.S. provisional application Ser. No. 60/294,724, filed May 31, 2001, the contents of all applications are hereby incorporated by reference in their entirety. This application is related to U.S. Ser. No. 10/160,604, filed May 31, 2002, currently copending, the contents of which are hereby incorporated by reference in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support under Grant (Contract) No. DE-AC03-76F00098 awarded by The United States Department of Energy. The government has certain rights to this invention.

BACKGROUND OF THE INVENTION

Since the first introduction of polymer electrolytes as a new class of solid electrolyte for energy storage applications, studies of all solid polymer electrolytes with ionic conductivity of 10^{-5} – 10^{-2} S/cm at ambient temperatures have received much attention owing to the potential applications in various electronic devices. Most of the previous efforts were based on the poly(oxyethylene) complexes with inorganic salts such as LiClO_4 , LiSO_3CF_3 and most recently, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, these systems are often denoted as binary electrolytes as both anion and cation contribute to the ion transportation. To achieve the practical applications of polymer electrolytes, the polymer has to satisfy several rigorous requirements: (1) bear strong ion coordinating sites to solvate inorganic salts, (2) must be amorphous with substantial segmental flexibility, (3) have durable mechanical and electrochemical stability for specific application environments. Numerous attempts have been tried to increase the conductivity by making PEO derived polymers, such as block copolymers, comb-branch polymers containing methylated poly(ethylene glycol) side chains, polymer networks and adding plasticizer or additives to break down the crystalline phase, which is detrimental to the transportation of charge carriers. In all these cases, however, the essential problem related to the efficiency of rechargeable polymer lithium batteries, i.e., polarization and very low Li^+ transference number is inevitable with a binary salt electrolyte. It is, therefore, desirable to properly design and synthesize polymers with the anion attached covalently to the polymer chain. The instant invention solves the aforementioned problems. Compared with binary systems, single-ion conductors show constant dc conductivity during dc polarization and shall have Li^+ cation transfer number of 1. Normally, single-ion conductors have much lower conductivity than binary salt electrolytes under the same conditions, in the range of 10^{-8} to 10^{-6} S cm^{-1} at 25° C. for alkali metal cations, due to the ion pairing to the immobile anion. It is therefore necessary to develop new materials with improved conductivity, e.g., 10^{-4} S cm^{-1} at room temperature, if they are to be used for lithium rechargeable batteries.

Hyper-comb-branched polymer conjugates are known in the art, for example U.S. Pat. No. 5,919,442 to Yin et al. Therein are described a class of hyper comb-branched polymers conjugates with carrier materials. This reference is incorporated herein by reference in its entirety.

A number of analyses of the operation of ionically conducting polymer membranes in lithium batteries have concluded that there are significant advantages if the lithium ion transference number is equal to one. In a lithium battery there are reactions for the cations at both electrodes but not for the anions. For a binary salt-polymer system, this will result in the build-up of concentration gradients across the cell, which cannot be relaxed rapidly by the diffusion of the salts. The cell will then exhibit concentration polarization resulting in loss of voltage on discharge and possible irreversible damage on charge. Concentration polarization also limits the thickness of intercalation electrodes that may be used thereby seriously reducing the energy density of the battery. Other groups have also postulated that a non-unity transference number of the electrolyte is one of the causes of dendrite formation, a phenomenon which leads to failure of the battery. Thus, the instant invention solves many problems by preparing a polymer electrolyte with a transference number equal to one—a single-ion conductor.

To prepare a single-ion conductor material, it is necessary to immobilize one of the ions on the polymer material. For a lithium ion single-ion conductor the anion is covalently fixed to the polymer. The best known single-ion conductor is Nafion® which is a perfluorinated polymer with side-chains to which are connected sulfonate groups. Ordinarily, the cations are hydrogen ions and the membrane is used in applications such as fuel cells. The hydrogen ions may be exchanged for lithium ions and the resulting membrane used in a lithium battery.

Several problems are present with this prior art system: the membrane must be used in a dry form to minimize reaction with lithium. The resulting conductivity is rather low as the lithium ions apparently ion-pair rather strongly to the sulfonate ions thereby reducing the mobility. The perfluorinated membrane is inherently unstable to lithium metal. The membrane is also not prepared with sufficient purity for use in lithium batteries. Other groups have attempted to prepare lithium ion single-ion conductors by incorporation of the anions into the backbone of a polyether polymer. Unfortunately, this results in a low conductivity as the cation is trapped by ion-pairing. Attachment of sulfonate or other anions to comb-branch polymers has been attempted. One method has been to use a grafting reaction where an anion-containing side-chain is reacted with a polyphosphazene chloride backbone. The drawbacks with this method have been the use of the polyphosphazene backbone which is inherently unstable to lithium and the lack of control of the grafting reaction which can leave reactive groups on the polymer that interfere with the lithium electrochemistry. Other methods have been to prepare a monomer that contains the anion-containing side chain and then polymerize. The polymerizable group usually must be reacted by a radical method as anionic or cationic methods are interfered with by the ionic group in the monomer. The types of polymerizable groups that are usually employed are acrylate, methacrylate and styrene. The resulting polymer backbone is unstable to lithium and also may restrict the polymer properties due to inherent stiffness of the backbone.

SUMMARY OF THE INVENTION

The invention described herein illustrates the synthesis, characterization, and electrochemical response of a new type of single-ion comb-branch polymer electrolytes. These are defined as a polymer electrolyte with a transference number equal to one.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be readily understood by the following detailed description in conjunction with the accompanying drawings: