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PERFORMANCE ANALYSIS POLYMER FOR BATTERY

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Abstract: Ion conducting polymer is the materials which exhibit high ionic conductivity, typically in the range of 10-5 to 10-1 S cm-1 and negligible electronic conductivity. These solids are also known as solid electrolytes, or fast ion conductors. The development of solid electrolytes has been driven by their tremendous technological applications in the areas of energy storage, energy conversion and in the field of environment monitoring. These materials are used as electrolytes and electrode separators in various electrochemical devices like, fuel cells, batteries, super capacitors, sensors, etc. The proton (H+) conducting polymer electrolytes have their possible applications in the various electrochemical devices like, fuel cells, batteries, super capacitors, sensors, etc however, they have largely been studied for their applications focused towards the development of low and moderate temperature fuel cells. Proton batteries are one of the other possible applications where polymer electrolytes can be used. But this application has not yet received considerable attention. The scarce reports appearing in the literature on the proton batteries indicate that these batteries may be considered as yet another potential alternative to the lithium ion batteries primarily because of small ionic radii of H+ ions, like Li+ ions, which makes them suitable for better intercalation into the layered structure of cathodes. The low cost of electrode and electrolyte materials used for proton batteries, and also no safety issues associated with them, are some of the important merits which support more research in this area.

INTRODUCTION

Ion conducting solids are the materials which exhibit high ionic conductivity, typically in the range of ~ 10-5 – 10-1 S cm-1, and negligible electronic conductivity [1]. These solids are also known as solid electrolytes, or fast ion conductors. The development of solid electrolytes has been driven by their tremendous technological applications in the areas of energy storage, energy conversion and in the field of environment monitoring. These materials are used as electrolytes and electrode separators in various electrochemical devices like, fuel cells, batteries, super capacitors, sensors, etc. By virtue of being a solid, solid electrolytes possess numerous advantages over liquid electrolytes like, absence of liquid containment and leakage problem, ability to operate with highly reactive electrodes over a wide range of temperature, and the possibility of miniaturization [2]. The ion transport in solid electrolytes is governed by some structural and nonstructural properties like, crystal structure, lattice arrangement, mobile ion concentration, size of the mobile ions, ionic polarizability, ion-ion interaction, ion interaction with the supporting matrix, number and the accessibility of occupancy sites, ion conduction pathway etc [3]. On the basis of their microstructure and the physical properties, the solid electrolytes are classified into four major categories:

1. Framework crystalline solid electrolytes

2. Amorphous-glassy solid electrolytes
3. Composite solid electrolytes
4. Polymer electrolytes

Out of the above four categories, polymer electrolytes are one of the most widely studied solid electrolytes. The film formability with desirable mechanical, thermal and electrochemical stability makes polymer electrolytes more attractive than the conventional liquid electrolytes and the brittle crystalline/polycrystalline, composite, and glassy solid electrolytes. Innumerable amount of work has been done on polymer electrolytes in the last few years which are excellently covered in several reviews [4-12]. The polymer electrolytes are further classified as (a) Conventional dry solid polymer electrolytes, (b) Plasticized solid polymer electrolytes, (c) Rubbery electrolytes, (d) Polyelectrolyte's, (e) Gel polymer electrolytes, and (f) Composite polymer electrolytes.

The conventional dry solid polymer electrolytes (SPE) are basically the polymer-salt complexes prepared by dissolving suitable ion donating salts/acids into high molecular weight polymers which act as a host. Examples of such host polymers are polyethylene oxide (PEO), polypropylene oxide (PPO), polyvinyl pyrrolidone (PVP) etc. The ion transport in these polymer electrolytes is governed by local relaxation as well as segmental motion of the polymer chains which are more favored by high degree of amorphicity of the host polymers [13, 14]. But, many host polymers are partially crystalline in nature which is an unfavorable property for achieving high ionic conductivity. Plasticization is one of the most adopted approaches used to suppress the crystalline of polymer electrolytes. In the plasticization, a substantial amount of a liquid plasticizer, namely, low molecular weight poly(ethylene glycol) (PEG) and/or aprotic organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), diethylene carbonate (DEC), dimethylsulfoxide (DMSO), etc is added to the dry SPE matrix. These polymer electrolytes fall in the category of plasticized solid polymer electrolytes. The addition of the liquid phases in the SPEs leads to the decrease in the crystallinity and the glass transition temperature of the host polymer and promote the segmental motion of the polymer chains, which, in turn, results into the higher ionic conductivity of the plasticized polymer electrolytes at ambient conditions. The high dielectric constants of the organic plasticizers like EC and PC also help in dissociation of ion aggregates, i.e. create more free ions, which further results into the higher electrical conductivity of the plasticized polymer electrolytes [15, 16]. Rubbery electrolytes are "polymer-in-salt" electrolyte systems, which are prepared by addition of small amount of high molecular weight polymers into a relatively larger amount of salts. The low amount of polymer leads to the formation of rubbery material with low glass transition temperature [17]. Polyelectrolyte is another category of polymer electrolytes in which polymers possess ion generating groups attached to their main chain. The most important and well known product of this class is Nafion. The Nafion membranes produced by DuPont are currently in use in portable fuel cell applications [18]. These membranes exhibit high proton conductivity, good chemical stability and mechanical integrity. Another category of polymer electrolytes is "Gel polymer electrolytes (GPEs)".Gels, in general, are defined as the solids with continuous liquid phase enclosed into a continuous solid skeleton. In GPEs, liquid phases are normally the organic liquid electrolytes, which are obtained by dissolving ion donating salts into the organic solvents/plasticizers, entrapped into the solid polymer network which provides dimensional stability to gel electrolytes [19]. It is observed that the larger amount of liquid electrolyte present in the polymer matrix gives rise to better ionic conductivity but diminishes the mechanical integrity of GPEs. Therefore, in order to improve the mechanical integrity, GPEs are dispersed with micro- and nano-sized ceramic fillers like SiO_2, Al_2O_3, TiO_2, $BaTiO_3$ etc. It is found that the dispersion of ceramic fillers not only improves mechanical strength but also improves the electrical conductivity of the GPE systems [20-24]. This category of polymer electrolytes is named as Composite polymer electrolytes. The dispersion of ceramic fillers has proved its worth in almost all the classes of polymer electrolytes which are often named as, composite dry SPEs, composite plasticized SPEs, composite polyelectrolyte, and composite GPEs. Polymer electrolytes support variety of ions, like Li+, H+, Na+, K+, Mg++, Cu++ etc, for transport. A large number of such polymer electrolytes have been developed in view of their various applications. The proton (H+) conducting polymer electrolytes have their possible applications in the various electrochemical devices like, fuel cells, batteries, super capacitors, sensors, etc [25-31], however, they have largely been studied for their applications focused towards the development of low and moderate temperature fuel cells. Proton batteries are one of the other possible applications where polymer electrolytes can be used. But this application has not yet received considerable attention. The scarce reports appearing in the literature on the proton batteries [26-29] indicate that these batteries may be considered as yet another potential alternative to the lithium ion batteries primarily because of small ionic radii of H+ ions, like Li+ ions, which makes them suitable for better intercalation into the layered structure of cathodes. The low cost of electrode and electrolyte materials used for proton batteries, and also no safety issues associated with them, are some of the important merits which support more research in this area.

The aim of the present work is directed towards performance and analysis of proton (H+) conducting polymer electrolyte membranes and their applications in proton batteries.

EXPERIMENTAL

Two kinds of cells were used in this study. The first one was made of glass. Both electrodes were hung with clips, and immersed in electrolyte solution (Fig. I (A)). Effect of additives in A1 substrates on cyclability was examined with the cell. The second one was made of P.T.F.E. Diameter of the electrodes was 9mm. Current collector was made of expanded stainless steel. We used the cell for cycle life test of Li-AI-Mg//PAn cell.

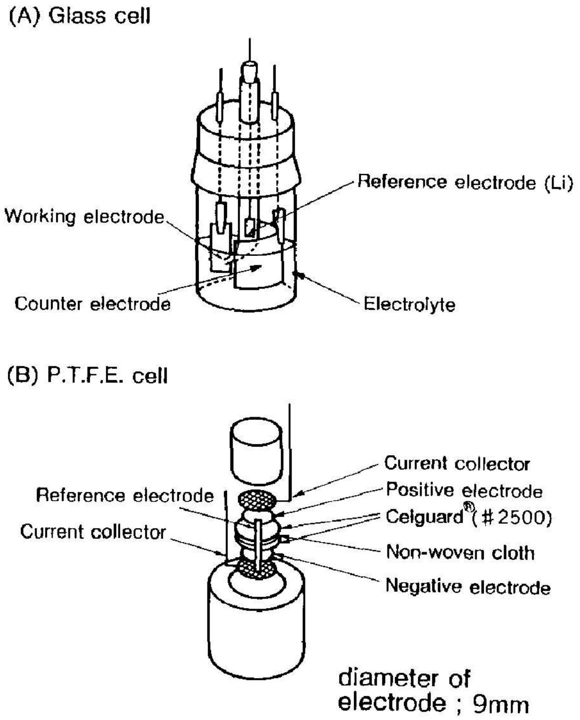

Fig. I. Schematic illustrations of cells used in this study.

Polyaniline was prepared by chemical polymerization with (NH4)2S208 in an aqueous medium. A positive electrode was prepared by mixing of PAn with 10wt% of carbon black and 10wt% of P.T.F.E. followed by molding into a disk which had a diameter of 9mm. A negative electrode was prepared by plating of Li on a substrate made of A1 alloy. Composition of alloys tested in this study was shown in TABLE I. Electrolyte solution was prepared by dissolving LiBF4 in the mixture composed of propylene carbonate(PC) and 1,2-dimethoxyethane (DME)(1:1, by volume).

Table 1. Compositions of Al alloys tested in this study.

AA code		Contents (wt %)							
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	
PURE Al	-	0.01	0.02	0.002	-	-	-	-	-
Al-Cu	2011	0.35	0.45	5.38	-	-	-	-	-
Al-Mg	5052	0.11	0.19	0.025	0.07	2.3	0.2	0.018	0.03
Al-Mg	5083	0.09	0.19	0.028	0.63	4.24	0.18	0.023	0.004
Al-Zn	-	0.09	0.18	0.023	0.43	1.38	0.11	4.6	0.013

RESULTS

Cyclability of Li//AI half cells using various A1 alloy substrates Cyclability of the cells was examined at 2.5mA/cm 2 of current density for plating and stripping.

Fig. 2. Cyclability of Li//AI and Li//AI-Mg half cells. Plating conditions: 2.5mA/cm 2 for 30min, stripping conditions: 2.5mA/cm 2, 1.0V (vs. Li/Li +) cut off, utilization: 160C/g(4.5atom% of Li/AI in substrate)

Contents of plated Li on A1 substrates were 160C/g-substrate in each cycle, which corresponded to 4.5atom% of Li per A1 in substrate. Stripping was terminated when potential of the working electrode reached to 1.0V vs. Li/Li + reference electrode in each cycle. Among the tested additives shown in TABLE I, Mg brought great improvements on cyclability of the half cell as shown in Fig. 2.

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