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FUTURE PROSPECTS OF POLYMER ELECTROLYTES

Chemistry

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ABSTRACT

The need for rechargeable batteries leads to the discovery of polymer electrolytes. These batteries are lighter and safer compared to existing liquid based batteries. Tremendous research is going on developing of polymer electrolytes which have better shelf life and is maintenance free. Also, the focus is on biodegradable batteries such that environmental impact of batteries is greatly reduced. In prospect of this, natural polymers electrolytes are being proposed. This paper studies the ionic conductivity of some of the natural polymer electrolytes which can lead to development of 'green' batteries.

1. Introduction

The use of electrochemical storage devices is increasing day by day. These find applications in electrochemical devices, super capacitors, fuel cells, and sensors [1-2]. All these storage devices comprise of three key components; a cathode, an anode, and an electrolyte. The flow of electron from anode to cathode accounts for the electric current while the cell is discharging. Reverse flow of electrons takes place when the cell is recharged. Batteries are of two kinds; primary and secondary. In case of former, the flow of electrons during recharging is not reversed and hence cell can only be used once. While in secondary batteries, the capacity of the cell can be restored during recharging [3]. With the development of technology, the use of mobile phone, mp3 players, solar cells, and electric vehicles is been increasing day by day. Hence, the development of secondary batteries is considered more important than primary batteries. The performance of these cells largely depends upon the properties of electrolyte being used. Researches have been carried out on development of different polymer electrolytes. The initial discovery was done by Wright et al. [4-5]. He reported the ionic conductivity in solid polymer electrolytes based on the complex of polyethyleneoxide (PEO) and alkaline metals salts.Other potential polymer hosts include polyacrylonitrile (PAN) [6], poly vinylchloride (PVC) [7], polymethylmethacrylate (PMMA) [8], and polyvinylidene fluoride (PVdF) [9]-[11].Lots of effort is being done onthe electrochemical preparation of polymer.

The greatest challenge is to increase the shelf life of the battery and make battery maintenance free. Thus rechargeable batteries with high power and high specific energy that provides good metal surface stability and high electrochemical stability are expected [3].

The electrolyte should have following features to be used in electrochemical devices:

- It should be capable of providing ionic contact between electrodes when the cell is functioning
- It should be capable of avoiding short circuit by assuring separation of positive and negative electrodes.

It is very essential to understand the ion transport mechanism in solid polymer electrolyte. It is based on interaction between the solid polymer matrix and metal ions [12]. A metal salt MX dissolved in polymer host results in formation of ion pair [MX].The association between the salt and polymer solvent is greatly influenced by the dielectricconstant of the solvent. The aggregation of the ion pair also takes place such as formation of large size [MX2]+. However, such kinds of aggregations lower the mobility within the polymer electrolyte hence affecting the ionic conductivity. Ion transport mechanism in polymer electrolytes are closely related to the segmental motion of the polymer host.

The initial discovery of polymer electrolyte started with solid polymer matrix in which macromolecular polymers such as PEO, PAN, and PMMA are dissolved in metals salt containing ions. The advantages of solid polymer electrolyte over the already used liquid electrolyte are numerous. Some of the important advantages with SPEs are: non-volatile, no leakage, light weight, no decomposition on electrode, durability of cell, better shock resistance, flexible shape, and enhanced safety [13].

However, the ionic conductivity in these types of polymers was poor due to the crystalline nature. Thus, there was a need to find alternatives which could increase not only conductivity of the polymer electrolyte but also the shelf life and electrode-electrolyte interface.

One of the methods to achieve this was addition of plasticizers. These are the low molecular weight polymers which are capable of introducing amorphicity in the polymer electrolyte. Along with amorphous nature, the modification also alters the glass transition temperature (Tg) of electrolyte. The decrease in Tg is proportional to increase in mobility of polymer host and consequently the ionic conductivity of the electrolyte is improved [14].

Next, fillers are added to the polymer electrolyte system comprising of polymer host, metal salt, and plasticizers. The fillers basically increase the mechanical strength of the electrolyte [15]. These types of polymer electrolytes are defined as composite polymer electrolytes. Recently, studies on CPEs have shown the promising results for them to be used as electrolyte for practical applications [16-18].Of the different types of polymer electrolytes, CPEs are widely studies and are found to be promising alternative to liquid electrolytes. Studies have shown polymer hosts such as PEO, PAN, and PMMA have shown good ionic conductivity as polymer electrolyte [19].

2. Need for Natural Polymer Electrolytes

The depletion of finite sources of materials has increased the interest of researchers in exploring natural polymers for use as electrolyte. Natural polymers, also known as biopolymers, has decreased impact on environment in terms of storage and discarding. Being biodegradable, biopolymers provide essential nutrients, through decomposition process, to the soil in carbon cycle. The use of natural polymers have also accounted for low cost productivity of the electrolyte. Studies [20] have shown that use of natural polymer composites have resulted in decrease of energy of polymer by 20 MJ/kg. Consequently, this result in reduction of 1KJof CO_2 thus reducing the environmental impact by 20%.

Plasticization method can be employed to natural polymers as well to enhance the properties of the electrolyte. Singh et al [21] have

found that the introduction of hydroxypropyl group to the starch have resulted in increase in amorphous phase. In other studies, water and glycerin, as plasticizers, are blended with starch. The polymer-plasticizer and polymer-polymer interactions form hydrogen bonding and van der Waals forces [22]. Many other natural polymers have shown potential to be used as an electrolyte.

The next section of this paper describes some of the natural polymer based electrolyte and their properties.

2.1 Natural polymer : Cellulose

Cellulose is a promising polymer host for solid polymer electrolytes due to it film forming ability, mechanical stability and rich nature [23]. The study of Nest et al have shown that cellulose based electrolyte, hydroxymethyl cellulose and hydroxypropyl cellulose, is obtained by grafting these polymers with diisocynate [24].

Different types of polymer matrix depending upon the structure and molecular weight of polymer and form of isocyanate. In research [25] clear films of hydroxyethylcellulose(HEC) were obtained by grafting HEC with PEO and isocyanates, and added $LiClO_4$. The ionic conductivity of 2.08×10^{-5} S/cm at 40 °C was obtained [26]. In another research [27] ionic conductivity of HPC–PEO polymer matrix with $LiN(CF_3SO_2)_2$ was found to be around 10^{-4} S/cm.

The cellulose based polymer electrolyte have shown great improvement over the years, still the ionic conductivity is not optimum to be used for practical applications.

2.2 Natural Polymer: Chitosan

Chitosan is the most researched polysaccharide. The optimal properties exhibited by chitosan are its biocompatibility and bioactivity, and is widely used in pharmaceutical and industrial applications [28,29]. Protonic battery based on chitosan powder, ammonium nitrate (NH_4NO_3) salt and ethylene carbonate (EC) plasticizer in acetic acid solution was formed. The battery showed an ionic conductivity of 10^{-3}S/cm at 70% EC [30]. In a study by Pawlicka et al the effect of different plasticizer such as glycerol, ethylene glycol, and sorbitol on chitosan was studied. The results have shown that the ionic conductivity of 9.5×10^{-4} S/cm at room temperature and 2.5×10^{-3} S/ cm at 80 °C were obtained. [31]. In a recent study, ionic conductivity of $2.15 \pm 0.47 \times 10^{-4}$ S/cm with 40 wt% glycerol [32] was obtained for chitosan-based electrolyte doped with NH_4Br and glycerol. Research is still being carried on to obtain good ionic conductivity with chitosan.

2.3 Natural Polymer: Starch

Starch like cellulose can be obtained from easily available natural resources. The research [33] showed that amylopectin- starch - polypropylene oxide –diisocyanate matrix exhibit good mechanical stability and amorphous nature. The ionic conductivity increases from range of 10–5 to 10–3 S/cm. Attempts were made to increase the ionic conductivity of starch- based polymer by complexation with ammonium nitrate [34] and NaI [35]. In the recent study, Glutaraldehyde (GA) crosslinkedwith potato starch, sodium iodide (NaI), in methanol showed ionic conductivity of 10^{-3} S/cm [36].

Many more natural polymers have been studied and an improved conductivity has been reported.

Table 1.1summarizes important natural polymers electrolytes with their composition and ionic conductivity.

Natural Polymer	Composition	Ionic Conductivity	Reference
Natural Rubber	49% methyl-grafted natural rubber (MG49) prepared by dissolving ammonium triflate ($NH_4CF_3SO_3$) in propylene carbonate (PC)	Highest conductivity of liquid electrolyte was 3.6×10^{-3} S/cm and PGEs was 2.9×10^{-2} S/cm	[37]
Agar	Agar- Acetic acid, Agar- Lactic acid, Agar- LiClO4, Agar- KClO4	6.54×10^{-8} S/cm 9.12×10^{-8} S/cm 3.53×10^{-8} S/cm, 2.24×10^{-8} S/cm	[38]
Pectin	Pectin and glycerol and addition of $LiClO_4$	4.7×10^{-4} S/cm at room temperature for the sample with 68 wt.% of glycerol	[39]
Xanthan Gum	Xanthan gum based gel electrolyte containing NH_4Cl salt	Maximum conductivity of 86 mS/cm	[40]
Amylopectin	Amylopectin-rich starch plasticized with glycerol	Ionic conductivity of $3.0x\ 10^{-5}$ S/cm	[41]
Sago Gel	Native sago with potassium hydroxide (KOH) aqueous	Ionic conductivity of $(4.45 \pm 0.1) \times 10^{-1}$ S/c m with 6 M KOH	[42]
Gelatin	Gelatin-Glycerol-CH_3COOH Gelatin-Glycerol-$LiClO_4$ Gelatin-Glycerol-$LiBF_4$	$4.5\ X10^{-5}$ S /cm $1.05\ X10^{-5}$ S /cm $1.0\ X10^{-5}$ S /cm	[43-45]

3. Conclusion & Future Prospects

Natural polymer based electrolytes are environmentally friendly and are cost effective. Many of the properties of natural polymer electrolyte have been improved by using plasticizers. However, as studied by many researches the ionic conductivity is not obtained to required level for practical applications. Research should focus on developing non-aqueous based natural polymer electrolyte system so that it is maintenance free and has increased shelf life. It is required to give more attention in field of natural polymer electrolytes so that in near future green batteries are used in almost all electrochemical devices.

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