Application of poly (2-hydroxyethyl methacrylate) gel electrolyte in electrochemical device: An Overview.

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Abstract  
This paper reviews the electrochemical and physical properties of polymer electrolyte for application in the electrochemical device. The current review is mainly focus on the Poly (2-hydroxyethyl methacrylate) (PHEMA) material as function of electrolyte. The development, ionic conductivity, morphology, porosity and application of this electrolyte material are reviewed. In this review, the performance of a few promising electrolytes used in electrochemical device is also discussed and compared.

Keywords: gel electrolyte, PHEMA, conductivity, porosity, application.

Introduction  
Nowadays, the electrical properties of the solid polymer electrolyte (SPE) and gel polymer electrolyte (GPE) are the important aspects in the research activities for implementation in the lithium polymer batteries. This is because in many electrochemical devices it received a high deal attention of possible application [1]. In solid state electrochemical devices such as chemical sensor [2], solar cell [3], fuel cell [4], electrochromic devices [5], supercapacitor [6] and mainly lithium ion battery, gel polymer electrolyte (GPEs) have attracted much attention as electrolytes [7]. Gel polymer electrolyte is much safer than the conventional liquid electrolyte when use in lithium battery because it uses the polymer matrix to entrap liquid component [8]. GPEs also have higher ionic conductivity than the solid polymer electrolyte and higher stability than liquid electrolyte [9].

Poly(2-hydroxyethylmethacrylate) (PHEMA) is a Polymer that well known as hydrogels types [10]. On 1960, Wicherle and Lim were the first introduce the 2-hydroxyethyl methacrylate (HEMA) in contact lenses [11]. 2-hydroxyethyl methacrylate (HEMA) hydrogel has stronger mechanical properties than other polymer. It can be strengthened by bulk polymerization, copolymerization with hydrophobic monomers and rigid cyclic monomer modification methods [12]. This polymer also nontoxic and biocompatible [13]. The excellent mechanical properties and chemical stability of PHEMA has also by contribution in controlling the optical property of semiconductor nanostructure [14].

In previous study, Mohar et al., reported that PHEMA able to absorb large amounts (40-45%) of water [15] and have the degree of flexibility similar to the naturally occurring tissue that has higher water content which decreases potential irritation to surrounding membrane and tissues [16]. Besides, PHEMA renowned as hydrophilic which also function for many biomedicine application [16]. Hydrophilic polymer network is retaining a large volume of liquid in a swollen state and able to swelling or de-swelling reversible in water [17] but do not dissolve in water [18].

PHEMA has high solubility in organic solvent such as methanol and ethanol, while it partially soluble in water that leads to the swelling phenomena in water presence. This polymer will become soft and flexible in the swelled state, while quite brittle in the dry state [19]. This PHEMA was chosen as a copolymer. HEMA will provide structural stability and rigidity which in turn reduce the methanol permeability to prevent polymer solubility [4].

At room temperature, the PHEMA membrane can swell in water, sulfuric acid and ferric sulfate solution. The good
chemical stability, high biocompatibility and physicochemical properties belong to PHEMA make it widely used in the field of biomedicine [20]. The biomedical and pharmaceutical fields studies, poly(2-hydroxyethyl methacrylate) PHEMA is used for a variety of applications including soft contact lenses [21], drug delivery applications and thrombo and fibro resistant coatings [10, 22], PHEMA cryogel also can remove the anti-dsNA antibodies from systemic lupus erythematous (SLE) disease [23]. Fig 1 shows that the chemical structure component of the Poly (2-hydroxyethyl methacrylate) component.

Figure 1. Poly (2-hydroxyethyl methacrylate)

Ionic Conductivity
A major obstacle to utilizing solid polymer electrolytes or hole conductor materials in dye-sensitized solar cell (DSSCs) is the difficulty in achieving good pore filling of these solids into mesoporous TiO$_2$ [3]. The lower ionic conductivity of the gel polymer electrolyte of PHEMA perhaps due to inhomogeneous and unbalanced morphology in the electrolyte [24]. Besides, the concentration of each polymer in the materials may control the ionic conductivity of the electrolytes. When the amorphous phase is larger than the crystalline phase, the conductivity will be higher [25]. The variations of ionic conductivities for the composite polymer gel are listed in Table 1.

The four ultimate requirements must be achieved in membrane development which are good long-term, thermal and interfacial stability, stable mechanical properties stability and elasticity, reasonable conductivity (above 10$^{-5}$ Scm$^{-1}$), and simple preparation method. The existence of polymer will affect the mobility, conductivity and prepared a sample, but not influences the qualities of behavior of immobilized species [26]. Yang et al.[27] has successfully fabricated the membrane of poly(vinylidene fluoride)/poly(2-hydroxyethyl methacrylate) PHEMA/ LiClO$_4$ electrolyte. Fig 2 shows the scanning electron microscopy (SEM) having (a) (50/40/10), (b)(25/65/10) and (c)PHEMA. Fig 2a and 2b show the difference composition of PHEMA concentration with PVDF. Fig 2c is the image of pure PHEMA membrane that seems quite similar to Figure 2b which shows only one phase. PHEMA is an amorphous polymer while PVDF is a polymer with a high level of crystallinity

Morphology and Structure
The morphology and the structure of fabricated membrane also has big influence on the membrane performance in terms of ionic conductivity and permeability.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Conductivity ($\text{Scm}^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECH$_{15}$/PHEMA 68/32 IPN</td>
<td>2$\times$10$^{-2}$</td>
<td>[29]</td>
</tr>
<tr>
<td>HEMA-NPG- 1M LiClO$_4$/ EC:PC</td>
<td>4.32x10$^{-3}$</td>
<td>[30]</td>
</tr>
<tr>
<td>PWA/HEMA</td>
<td>1.4x10$^{-4}$</td>
<td>[24]</td>
</tr>
<tr>
<td>PVAHEMA-SiO$_2$</td>
<td>0.11</td>
<td>[27]</td>
</tr>
<tr>
<td>PHEMA/PVDF/ LiClO$_4$</td>
<td>1.2x10$^{-4}$</td>
<td>[25]</td>
</tr>
<tr>
<td>PHEMA/ETMEIM(HF)$_n$F N=0.6</td>
<td>2.3x10$^{-2}$</td>
<td>[28]</td>
</tr>
</tbody>
</table>
Figure 2. SEM image of the cryogenic fracture surface of (a) PVDF/PHEMA/LiClO$_4$ electrolyte (50/40/10), (b) (25/65/10), (c) PHEMA[25].

The concentration of monomer will affect the pore structure in the hydrogels. Hydrogel will become compact structures, having lower water content and small pore in the membrane when the concentration of the monomer increased[18]. PHEMA cryogels provides channels for the mobile phase to flow through, and they have large continuous interconnected pores (10-200µm in diameter) which are non-porous and thin polymer walls. PHEMA cryogel is sponge-like, opaque and elastic[23].

Application of Poly (2-hydroxyethyl methacrylate)

PHEMA is very important in macromolecular chemistry application. As reviewed, the number of applications of Poly (2-hydroxyethyl methacrylate) has been increase nowadays due to its properties such as easily polymerized, possess a hydrophilic pendant group and enable to form hydrogels[34].

Poly (2-hydroxyethyl methacrylate) also has been using in the fabrication of the chemical sensor. This sensor is fabricated via ink-jet printing process which is nanoparticle deposition and the subsequent nanoparticle functionalization with PHEMA polymer. This chemical sensor also adequate to detect the humidity and ethanol molecules with the range of 2000-20000 ppm in chemiresistor, chemi-capacitor or chemi-impedance sensor [35]. Besides, PHEMA also have been used for disposable amperometric sensors by modified with ferrocene functionalities as novel coatings for the development. This sensor function for process control, efficient devices for food and environmental clinical analyses[36]. PHEMA also has found to be film for mediated aerometric glucose biosensor. Due to the lower hydrophilicity and low mobility of VFc in the films, Fe/H$_2$-enzyme glucose oxide (GOD) biosensor films have the higher response to substrate compare to VFc/H-enzyme glucose oxide (GOD) biosensor film[37].

In Dye-sensitized solar cells (DSSCs) application, Poly (2-hydroxyethyl methacrylate) gel electrolyte also use as a counter electrode and imbibed gel electrolyte[31]. Base on Li et al studies, they fabricate quasi-solid state dye-sensitizer solar cells based on the polyaniline (PANi) absorb with poly(HEMA/CTAB) gel electrolyte. The successful synthesized gel has perform well by applying the unique absorption and interconnectivity between PANi and poly(HEMA/CTAB) with conversion efficiency 6.68%[32].

The extensive investigation on the usage of PHEMA hydrogels is as a protective anion exchange membrane on air electrode for the aqueous alkaline metal-air batteries. A high degree of intimacy between catalyst particles and the membrane is required to allow the oxygen diffusion during electrode operation, [29].

Another main application of PHEMA hydrogel is used in the preparation of transistor[38]. The main charge storage site of the electrons in PHEMA is Hydroxyl (-OH) group. PHEMA use for improving the memory effect in the pentacene-based organic thin film transistor (OTFT). The electron trapping and slow polarization of the dielectrics was develop ed to form memory effect[39].

Challenge

The most important requirement properties for the polymer gel electrolyte function is the immobilization of electrolyte [40]. The gel polymer electrolytes (GPEs) exhibit high ionic conductivity, usually over 10$^{-3}$ S cm$^{-1}$ at room temperature.
However, most of them often showed poor mechanical properties because the impregnation of a liquid electrolyte into a polymer matrix resulted in polymer softening. The poor mechanical properties may lead to the internal short circuit and safe hazards for battery[40].

Besides that, in the solar cell, they have some problems in the utilizing of solid polymer electrolytes or hole conductor material in dye-sensitized solar cell DSCC. This is because in the mesoporous TiO$_2$ layer, they have a difficulty in achieving good pore filling of these solids electrolyte [41].

Conclusion
As reviewed in this paper, the PHEMA is one of the known polymer in many application such medical, sensor, optical as well as electrochemical devices. This current review paper mainly focus on the application of PHEMA as electrochemical device. As mentioned earlier, the PHEMA has many advantages and but also possess some weaknesses. The main properties of PHEMA is water insoluble, flexible and capable to form gel membrane. The PHEMA proven can be used to increase the ionic conductivity of the membrane depending on its morphology and structure as reported by several previous studies. Several applications that involved PHEMA polymer has been discussed briefly in this review such as sensor, transistor and battery. Moreover, the challenges of PHEMA behavior in the gel polymer electrolyte also has been discussed shortly. Thus, further studies and investigation on this PHEMA polymer should be explored in the future to achieve the optimum properties and good performance in many application especially in electrochemical devices.

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