

The Study of Different Applications of Polyelectrolyte its Polymer

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ABSTRACT

Man focus on these different types of polymer electrolytes, recent approaches and technological applications of polymer electrolytes. The report first discusses the characteristics, advantages and applications for three types of polymer electrolytes: gel polymer electrolytes, solid polymer electrolytes and composite polymer electrolytes. Next, we discuss the features and performance of different polymer hosts based on some important and recently published literature (Ramesh, *et. al* 2016). Recent progress of some approaches used in improving the performance of the polymer electrolytes is highlighted. It is also stressed that the technological advancement in the polymer electrolytes plays important role in the development of energy converting and storing systems in future.

Key word: Application, Polymerelectrolyte, Fundamental, Ionic conductivity and Polymer hosts

INTRODUCTION

In recent time, Polymers are widely used because of their deformability, low density, and extensive potential for tailoring macroscale properties through chemical composition, molecular architecture, and processing. Polyelectrolytes are a particularly exciting subclass of polymers that are ionically charged. If this is sounding a lot like ionomers (as in the much-studied Nafion™), you're right! Those are a further subclass with < 15% of the monomers charged. Polyelectrolytes have unique mechanical, ionic, and electromechanical properties enabled by the interactions among the backbone charges and free ions contained within the polymer. The charges on the polymer influence backbone conformation, can act as crosslinks, and can drive formation of micelles that are vital both for mechanical properties and ionic conductivity. While we will focus on synthetic polyelectrolytes, it must be mentioned that polyelectrolytes are abundant in biology and are, for example, responsible for many of the pH dependent conformational changes in proteins (Hong *et. al* 2010, Silberstein & Boyce 2010, Luo *et. al* 2015, Liu *et. al* 2013, Zhang *et. al* 2020).

Polyelectrolyte's unique properties make them useful in a variety of applications including actuators, sensors, energy conversion technologies such as fuel cells and batteries, impact protection, drug delivery, and biocompatible electronics. For example, their high ionic conductivity and mechanical strength make them ideal ion exchange membranes for low temperature (~80°C) fuel cells. Dynamic ion bonds facilitate self-healing. For example, Surlyn™ will self-heal after a bullet passes through simply from the thermal energy provided by the bullet itself. Finally, their elastic deformability and ability to sustain ion gradients means that they are natural electrochemical actuators. In this journal club entry, we will focus on how polyelectrolytes behave mechanically in electric fields. While the ion transport properties of this material class are also quite interesting, we have decided not to discuss them here since there is an excellent recent imechanica blog on the ionotronics of hydrogel polyelectrolytes (Varley 2007).

The ongoing efforts to replace liquid electrolyte have led to the development of polymer electrolyte battery. Polymer electrolyte battery is not only well-known for its safety features but for its high power density, flexibility, plasticity of size and shape (Scrosati 2001, Vincent & Scrosati 2000). In addition, it also play a key role as binder for the electrode as it simplifies the fabrication process of battery cell. It is anticipated that the reduction in power

consumption of electronics devices, and a thin film like solid polymer electrolyte will be adequate to power these devices. However, with the advancement of technology, the hunger for higher power density in portable electronics devices such as hand-phone has led to the requirement of high power consumption as a result of increasing functionality. Many strategies and approaches have been deployed to increase the ionic conductivity such as plasticizing the polymer electrolyte with small organic molecules e.g.s ethylene carbonate (EC) or dimethyl carbonate (DMC) which has high dielectric constant and low vapor pressure to address such need. However, minimal research on biodegradable polymer electrolyte is reported for the past decade. One of the primary concerns that discourage research in polymer electrolyte is believed to be due to the environmental impact it would bring if polymer electrolytes are used in large amounts (Wright & Br 1975). To address such concern, research on developing biodegradable polymer electrolyte using “ecomaterials” have become increasingly important with the aim to reduce the environmental impact (Fonseca *et. al* 2006).

The development of solid-state materials such as ceramic, glass, crystalline and polymer electrolytes initialled in the early 1970s (Ramesh S. & Liew C.W. 2010). Polymer electrolyte was first introduced by Fenton *et. al.* in 1973(Fenton DE *et. al* 1973), and the importance of its technological application was recognized in early 1980s(Shriver DF& Bruce PG 1995). In the past three decades, the development of new PEs has received attention from many researchers due to their potential applications in electrochemical/electrical power generation, storage and conversion systems.

Polymer electrolyte (PE) is a membrane composed of dissolution of salts in a polymer matrix with high molecular weight (Ramesh S. & Lu S.C. 2012). This solid solvent-free system possesses ionic conduction property and therefore is widely applied in electrochemical devices such as solid-state batteries and rechargeable batteries, especially lithium ion batteries. In recent years, PEs have other prospective applications in advanced electrochemical, electrochromic and electronic devices such as supercapacitors, fuel cells, dye-sensitized solar cells, rechargeable batteries, electrochemical sensors, analogue memory devices and electrochromic windows(Bruce PG 1995, Kim *et. al* 2004, MacCallum JR&Vincent CA 1987, Scrosati B 1993, Vincent CA 1987). List 1 summarized the properties, advantages and applications of the polymer electrolytes.

The development of solid-state ionic conductors, such as fast/superionic conductors, insertion compounds and polymer electrolytes, has created an upsurge of interest among the researchers (Ramesh *et. al* 2010). PEs are technologically evolved from polymer, liquid ionic conductor and solid-state ionic conductor. PEs can be prepared by dissolving metal salts in polar polymer hosts (Kim *et. al* 2004). The launch of PE as a new solid-state material has caused it to be widely employed as a building block for various electrochemical devices. Polymer electrolyte can also be used as a separator in a battery, and it also can be used to replace the liquid ionic solution (Ramesh &Lu 2012, Ramesh *et. al* 2014, Sanchez *et. al* 1998).

List 1: The properties, advantages and applications of the polymer electrolytes

Properties of PEs

Transparency

Solvent-free

Light-weight

Flexible

Thin-firm forming ability

High ionic conductivity

Easy processability

Wide electrochemical windows
Advantages of PEs
Prevent leakage
No internal shorting
Eliminate the use of corrosive solvent
No production of harmful gases
Application of PEs
Electrochromic window
Solid-state batteries
Solar cells
Fuel cells
Dye-sensitized solar cells
Electrocapacitors
Actuators
Electrochemical sensors
Analogue memory devices
High vacuum electrochemistry
Thermoelectric generators
Portable power sources
Start-light ignition
Electric vehicles
Thin credit cards
Mobile cellular phone
Laptop compute

TYPES POLYELECTROLYTES

1. SOLID POLYMER ELECTROLYTES:

The research on solid polymer electrolyte (SPE) was launched by Wright *et. al.* three decades ago (Wright PV 1975). Armand *et. al.* have verified the technological application of SPEs in electrochemical devices (Armand *et. al.* 1979). A “dry solid” polymer electrolyte based on PEO was the first SPE investigated (Fenton *et. al.* 1973). This is a solvent-free system where organic liquid is not used. The performance of this PEO-based SPE was unsatisfactory due to the poor ionic conductivity at room temperature (Ramesh & Liew 2012).

SPEs have been extensively studied in recent years because of their potential applications in many electrochromic and electrochemical devices, such as electrochromic windows, solid-state batteries, solar cells, fuel cells, dye-sensitized solar cells (DSSCs), electrocapacitors, actuators, electrochemical sensors, analogue memory devices, high vacuum electrochemistry, thermoelectric generators, portable power sources, start-light-ignition (SLI) and electric vehicles (EV) (Bruce 1995, Vincent 1987, Ramesh *et. al.* 2010, Gray 19991, Stephan 2006, Ahmad *et. al.* 2005, Liew *et. al.* 2012). The development of SPEs also found wide applications in many portable electronic devices, such as thin credit cards, mobile cellular phones and laptop computers (Gray 1991). Besides ionic conductor, SPEs also work as separator between electrolyte and electrode in cells or batteries, which eliminates the use of inert porous spacers. They also act as binders to facilitate the electrical contact with electrodes and this eliminates the need for high-temperature process as required in liquid electrolytes (Gray 1991).

2. POLY(ϵ -CAPROLACTONE):

Poly(ϵ -caprolactone) (PCL) has low glass transition temperature, is fully biodegradable, has excellent biocompatibility and bioresorbability, and this makes it popular in biomedical applications (Amass *et. al.* 1998, Coombes *et. al.* 2004). PCL exhibits excellent ionic

conductivity with the addition of ammonium thiocyanate (NH₄SCN) salt as a source of charge carriers (Woo *et. al* 2014).

3. POLY(ACRYLIC ACID):

PAA possesses superior mechanical strength, good processability and biodegradability (Kam W *et. al* 2014). PAA forms a stable complex with metals (Dasenbrock *et. al* 1998). The environmental friendly feature of PAA is vital and leads to popular applications in lithium-conducting PEs. Kam *et. al.* reported a PAA-based CPE doped by LiTFSI salt that achieved a good ionic conductivity at ambient temperature.

4. POLY(ETHYL METHACRYLATE):

In recent years, PEMA has started to gain popularity in the making of PEs membrane. It is a derivation of methyl acrylate polymers which can be used as host polymer to prepare some solid matrices (Ramesh *et. al* 2014). The large pendant group of PEMA makes it more flexible and perform better than another type of polymer, i.e. PMMA. Indeed, a polymer backbone with high conductivity and good flexibility is needed to prepare an SPE for various applications (Ramesh *et. al* 2014).

5. POLYMER HOSTS:

The preparation of PE required at least one host polymer acting as a base matrix prior to the addition of any other materials. Examples of host polymer that are commonly used in the preparation of PEs are poly(vinyl chloride) (PVC), poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), PEO, poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVdF), poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP), chitosan etc. (Stephan AM 2006, Yang *et. al* 2013). The polymer hosts generally used with repeat units and examples of polymer electrolyte complexes.

6. POLY(VINYL ALCOHOL):

PVA is a promising candidate for host polymer due to its inherent characteristics like good tensile strength, mechanical strength, non-toxicity, cost effectiveness, good optical properties, high temperature resistance and high hydrophilicity (Dasenbrock *et. al* 1998, Tang *et. al* 2008, Yang *et. al* 2009). The high hydrophilicity of PVA is due to the presence of a large extent of the polar hydroxyl group. Usage of PVA also provides other advantages like ease in preparation, high abrasion resistance, good flexibility and biocompatibility, excellent chemical and thermal stabilities (Lu *et. al* 2009, Qiao *et. al* 2009). Superior features of PVA such as high charge storage capacity, high dielectric constant and dopant-dependent electrical properties caused it to receive considerable research interest in the development of fuel cell and electrical double-layer capacitor (EDLC) (Hirankumar *et. al* 2005). Yang reported a study based on the PVA-KOH- H₂O system (Yang CC 2004). The relation between the ionic conductivity and the chemical composition was investigated. The results indicate that the ionic conductivity of the PVA-KOH system is strongly dependent on the composition of KOH and the water content in the film (Yang 2004).

7. COMPOSITE POLYMER ELECTROLYTES (CPEs):

One of the major reasons behind the poor ionic conductivity of polymer electrolytes has been attributed to the presence of ion-pairs (or ion-association) and ion triplets. This is due to weak dielectric constant of the host polymers (S.R. *et. al* 2009). Many approaches have been developed to avoid the occurrence of ion-ion association in polymer electrolytes. To solve

these difficulties and improve the qualities of SPEs, inorganic inert fillers with high dielectric constant has been lately suggested to be dispersed in PEs (Mulmi *et. al* 2009). Dielectric permittivity can be properly adjusted, simply by controlling the type and the amount of incorporated inorganic filler material. Ceramic materials, which are classified as inorganic fillers, are typically fragile and possess low dielectric strength (Kontos *et. al* 2007). Though, polymers have relatively low dielectric permittivity, they can undergo high fields, they are also flexible and easy to be processed. Therefore, by combining the advantages of these two materials, i.e., ceramic filler and polymer material, new hybrid composite materials with high dielectric constants can be fabricated (Thomas *et. al* 2010).

8. OTHER POLYMER HOSTS:

Many researchers discussed physical and electrochemical properties of other polymer host systems. The phase changes with respect to the dissolution of lithium salt in linear poly(ethylene imine) has been investigated by (Chiang *et. al* 1986). The studies also have been made on copolymer of EO-PO (Ishikawa *et. al* 1990), poly(ethers) (Peterson *et. al* 1992), poly(methoxy, ethoxy ethyl methacrylate) poly(MEEMA) (Immanuel *et. al* 1995) and ter-polymer of MMA-EO-PO (Wieczorek & Stevens 1997).

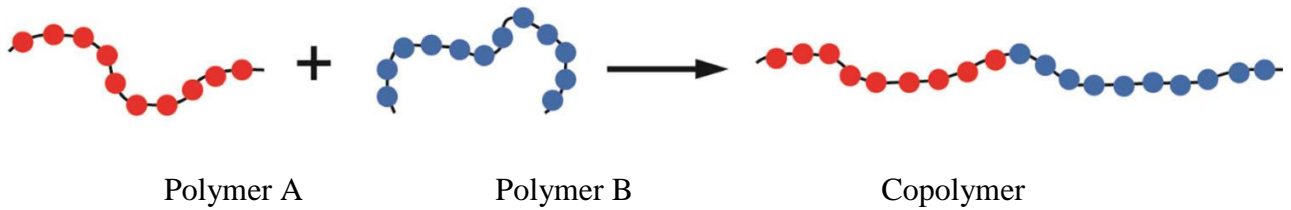
9. POLY(ACRYLONITRILE):

Among the polymer hosts studied, so far, the PAN based electrolytes offer a homogenous, hybrid electrolyte films in which the salt and the plasticizer were molecularly dispersed. Watanabe *et. al.* (Watanabe *et. al* 1982, Watanabe *et. al* 1983) used a combination of plasticizers EC and PC to plasticize PAN and complexed with LiClO_4 and they correlated with the mole ratio (plasticizer)/ (LiClO_4) of the gel electrolytes. The authors concluded that the PAN host is inactive in the ionic transport mechanism but acts as a matrix for structural stability.

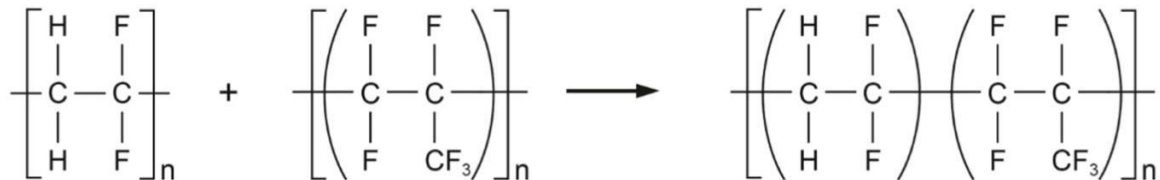
COPOLYMERS

Copolymer is a polymer prepared from at least two different types of monomers. Copolymers can be prepared by using the cross-linking method (Wen *et. al* 2003). PVdF-HFP is the most common copolymer that is prepared by co-polymerization of PVdF and HFP, as shown in Fig. 1. The copolymer exhibits better features compared with the monomers alone which could be attributed to the synergistic effects in the combined structure. A gel PVdF-HFP copolymer shows lower crystallinity, low glass transition temperature and better solubility in organic solvents compared with PVdF (Gozdz *et. al* 1994). A poly(1-vinylpyrrolidone-co-vinyl acetate (P(VP-co-VAc))-hosted GPE was prepared by incorporating the ionic liquid, LiTFSI and EMImTFSI (Saadum *et. al* 2014). Aihara *et. al.* made a plasticized copolymer of ethylene oxide and propylene oxide using cross-linking technique and applied it in a lithium battery (Aihara *et. al* 1997). A poly(acrylonitrile-co-methyl methacrylate) (P(AN-co-MMA))-based composite PE was prepared with plasticizers (EC-PC), lithium salt (LiClO_4) and silica as fillers (Lee K-H *et. al* 2000). A maximum ion conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature was obtained with 10 wt% silica. Higher silica contents lead to the decrease of ionic conductivity which could be attributed to the increase of viscosity of plasticizer-rich phase. A solid copolymer electrolyte consisting of epichlorohydrin and ethylene oxide exhibits a high ionic conductivity in KOH systems at room temperature. The applicability of the copolymer electrolyte of epichlorohydrin and ethylene oxide in electrochemical devices was tested. This copolymer demonstrated a good performance in a zinc/air primary cell and a nickel/metal hydride secondary battery (Vassal *et. al* 2000).

A



B



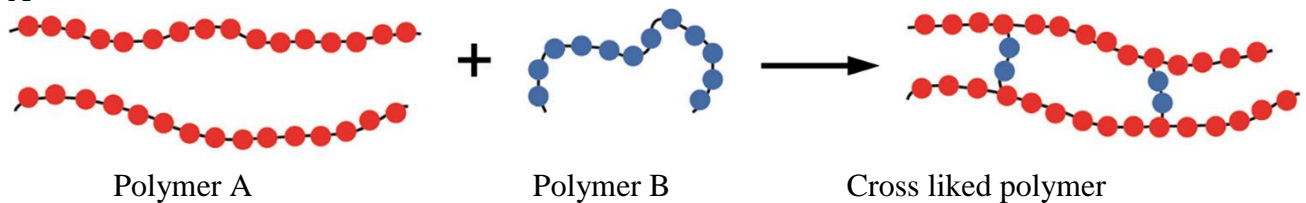
poly(vinylidene fluoride) hexafluoropropylene poly(vinylidene fluoride hexafluoropropylene)

Fig. 1: a Pictorial model of the preparation of a copolymer. bP(VdF)-HFP, an example of copolymer formed by PVdF and HFP

CROSS-LINKED POLYMERS

The high ionic conductivity of SPEs at low temperature is associated with the amorphous nature of the polymer matrix. The cross-linked PEs show good ionic conductivity at ambient temperature and exhibit fully amorphous feature (Nishimoto *et. al* 1999). In contrary, cross-linked polymer usually exhibits brittleness, low elasticity and processability (Wen Z *et. al* 2003) . Matsui *et. al.* have prepared a cross-linked PE of poly(ethylene oxide) 2-(2-methoxy ethoxy) ethyl glycidyl ether with and without allyl glycidyl ether, P(EO/MEEGE/AGE) complexed in LiN(CF₃SO₃)₂ salts (Matsui *et. al* 2001). Kuratomi and co-workers have developed a cross-linked copolymer of ethylene oxide and propylene oxide with LiBF₄ or LiN(CF₃SO₂)₂ salts (Kuratomi J *et. al* 2001) . The results demonstrate that LiN(CF₃SO₂)₂ exhibits better cyclability in lithium battery compared with LiBF₄. The concentration and types of lithium salts used are significant in determining battery performance. The study of a cross-linked of high molecular weight poly(oxy ethylene)s has been conducted and the new PEs show favourable ionic conductivity and good mechanical strength (Matoba *et. al* 2003). Another new CPE of chemically cross-linked poly(EO/PO)/(LiN(CF₃SO₂)₂) had been reported(Wen Z *et. al* 2003). Lee and co-workers have also reported a cross-linked composite PE by polymerizing alkyl monomer and polyethylene glycol dimethylacrylate (PEGDMA) in LiPF₆/EC(Lee KH *et. al* 2001).

A



B

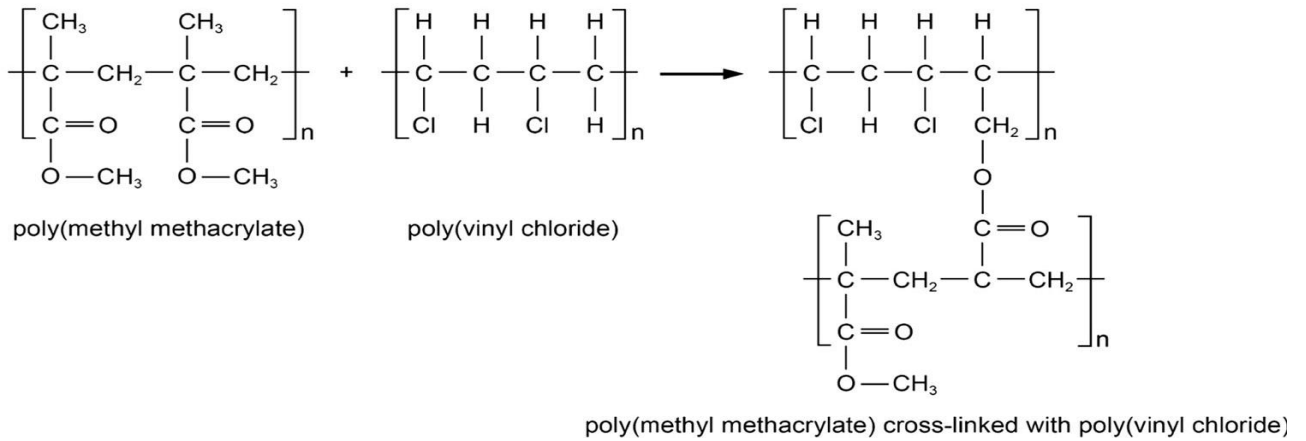


Fig. 2: a Pictorial model of A preparation of a cross-linked polymer. b Example of a crosslinked polymer formed by PMMA and PVC

APPLICATIONS

Fossil fuel is the major source of energy supplies for the past few decades. Fossil fuels are unrenowable and the combustion of fossil fuels releases hazardous pollutants which cause severe environmental, ecological and economical impacts in the future. A green and renewable power source becomes an attractive alternative source for energy (Winter & Brodd 2004). Recent developments of resource substituent and renewable energy leads to the advancement in the methods of generating, storing, retrieving and converting electrical energy (Shukla *et. al* 2000). Electrochemical energy production, storage or conversion systems include electrochemical capacitors and batteries (Winter & Brodd 2004). Fig. 3, 4, 5 and 6 display the basic operating mechanism for different electrochemical systems. All the systems share some common features, such as two electrodes acting as electronic conductors in contact with an electrolyte solution (ionic conductor). The electron and ion transports are separated and the energy-generating process takes place at the electrode/electrolyte interface (Winter & Brodd 2004).

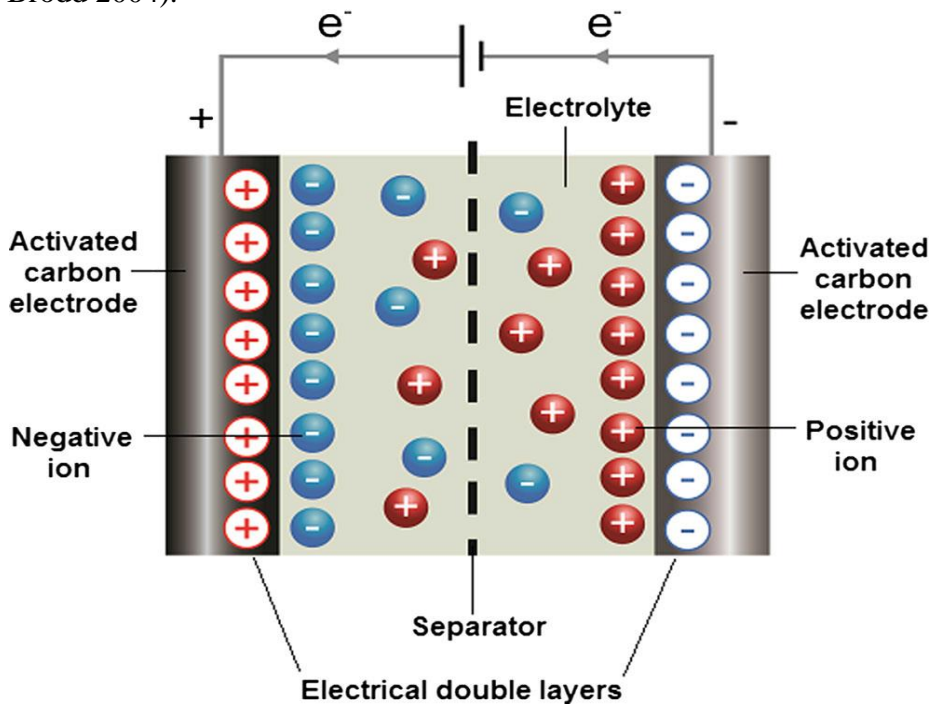


Fig. 3: Schematic cross-section of a typical electrical double-layer capacitor

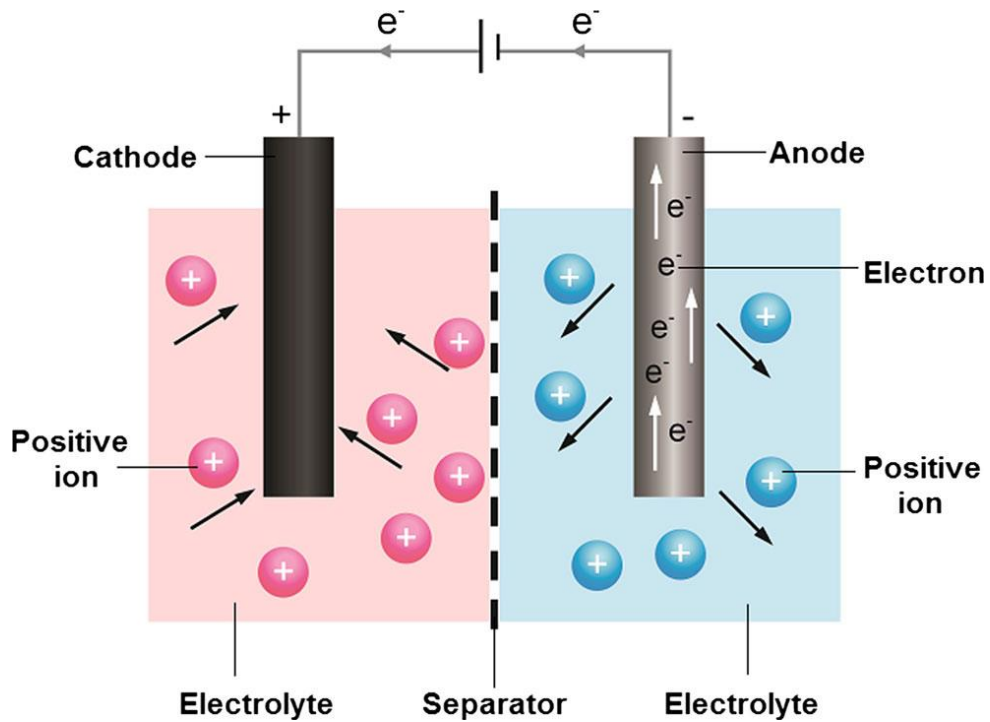


Fig. 4: Schematic cross-section of a typical battery

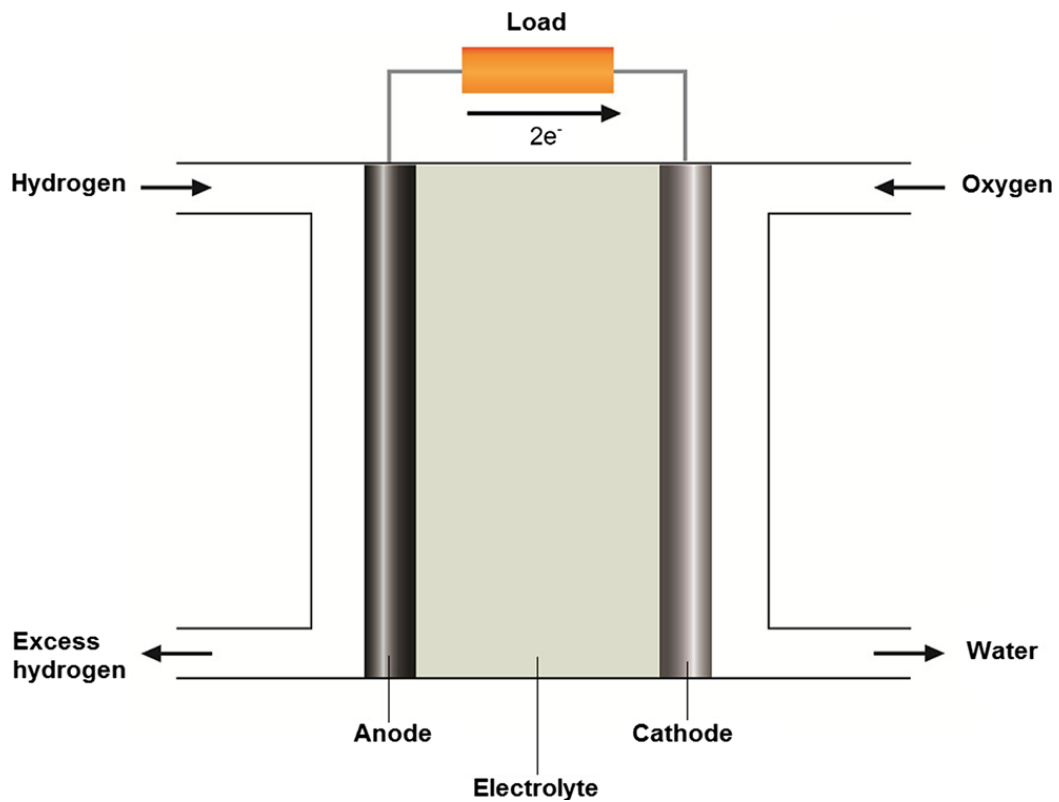


Fig. 5: Schematic cross-section of a hydrogen fuel cell

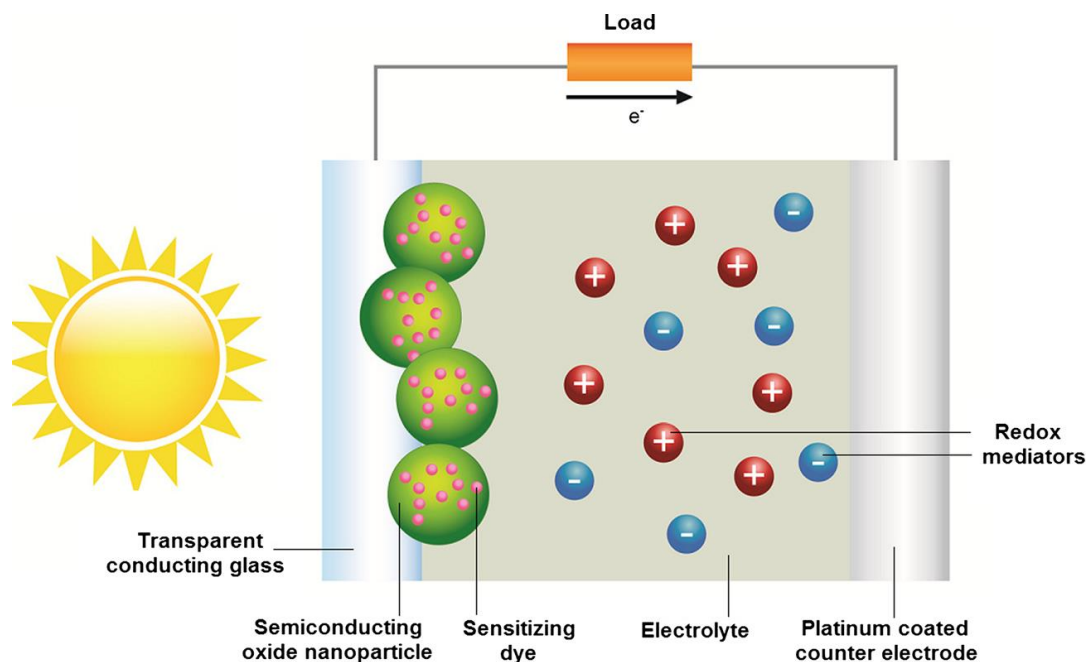


Fig. 6: Schematic cross-section of a typical dye-sensitized solar cell

SUMMARY

The different used of polymer electrolytes in many electrical, electrochemical and electrochromic devices have advanced many in recent years. More polymer hosts has been studied and reported in the literature, like as PEO, PMMA, PAN, PAA, PVdF, PVdF-HFP and PVC. The used of composite polymer electrolytes have been identified as a promising method to improve the electrolytes' properties. It is ionic conductivity of the dominant property of a PE and can be enhanced by increasing the amorphous proportion. The degree of crystallinity can be reduced by several physical/chemical treatments or doping with selected substances (Koh Sing Ngai *et. al* 2016). Many approaches has been applied to prepare the composite polymer electrolytes, and among the most commonly adopted are blending, crosslinking and Polymer electrolytes are technologically important in the development of electrochemical capacitors, batteries, fuel cells and dye-sensitized solar cells. Many reports have shown that the CPEs have advantages over conventional liquid electrolytes, especially in their conductivity, flexibility and safety in coming future.

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