High-Temperature PEM Fuel Cells

Subjects: Polymer Science

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This review summarizes the current status, operating principles, and recent advances in high-temperature polymer electrolyte membranes (HT-PEMs), with a particular focus on the recent developments, technical challenges and commercial prospects of the HT-PEM fuel cells. A detailed review of the most recent research activities has been covered by this work, with a major focus on the state-of-the-art concepts describing the proton conductivity and degradation mechanisms of HT-PEMs. Also, the fuel cell performance and the lifetime of HT-PEM fuel cells as a function of operating conditions have been discussed. In addition, the review will highlight the important outcomes found in recent literature about the HT-PEM fuel cell. The main objectives of this review paper will be as follows: (1) the latest development of the HT-PEMs, primarily based on polybenzimidazole membranes, (2) the latest development of the fuel cell performance and the lifetime of the HT-PEMs.

Keywords: Polymer electrolyte membranes ; High-temperature ; Proton conductivity ; Polybenzimidazole ; Fuel cell performance

1. Introduction

Sufficient access to clean energy sources is one of the ongoing key challenges for global development that directly impacts industrial development, economic growth, and human well-being. Historically, the energy sector is widely dominated based on fossil fuels (such as petroleum fuels, natural gas, coal, etc.) which are the primary source of carbon dioxide (CO_2) and the other greenhouse gases emissions to the environment. This has fundamentally driven a global climate change that has been accelerated over the past few decades and hence needs significant and immediate actions in order to alter both the energy sources and energy conversion techniques. There is a growing movement by the research and manufacturing communities to alleviate the impact of the petroleum-based economy by developing clean energy sources for implementing an alternative hydrogen-based economy [1][2][3]. Given the current environmental challenges associated with fossil fuels, fuel cell technology has been introduced as a promising, cleaner, high energy density, and more efficient power generation system [2][4][5]. Lately, polymer electrolyte membrane (PEM) fuel cells, which directly convert the chemical energy of hydrogen into electrical energy, have been predominantly developed as the most common commercial fuel cell [6][7].Hydrogen gas (as a fuel with the highest energy density) and oxygen (usually taken from air) are being used in a PEM fuel cell over the surface of electrodes to produce water through a few electrochemical reactions that are associated with the electrical power generation [8].

2. Desirable properties of PEMs

The PEM is the heart of the membrane electrode assemblies (MEAs) that are used for the fabrication of the PEM fuel cell stacks [9]. The PEM has a vital role in a fuel cell assembly by performing various functions such as being a carrier path for proton transport from the anode to the cathode side, a dense separation layer to block mixing the reactants, and an electric insulation layer between the anode and cathode. Many studies in the past few years have reported the enhancement of various functions of PEMs [10][11][12][13]. One of the key objectives for the PEMs development is to reduce the cells' total fabrication cost and improve their electrochemical performance and durability [14][15]. A desirable cost-effective PEM should exhibit an acceptable thermochemical and thermomechanical stability, low permeability to fuel and oxidants, high proton conductivity, high compatibility with the electrodes in an MEA, long durability, and low electro-osmotic drag coefficient [16].

3. Improving proton conductivity of the membranes

3.1. Effects of dopants and additives

Several dopants have been used to improve the proton conductivity of PEMs, especially PBI. The proton conductivity of PBI is very low, and it requires the incorporation of dopants, additives, etc. [17]. Full or partial protonation or deprotonation of the polymers happens depending on the concentration and chemical nature of the dopant [18]. PBI is an amphoteric compound and has both proton acceptor and proton donor sites [19]. A wide variety of acids and bases, such as H_2SO_4 [20], H_3PO_4 [21], NaOH [22], KOH [23], etc., have been used as dopants. Compared to the low-temperature cells, HT-PEMs require high-boiling dopants which can operate at elevated operational temperatures. Dopant concentration is a key parameter in improving proton conductivity, however, up to a certain amount. Excessive doping may deteriorate the conductivity. For example, acid doping with a high concentration (>11 $mol.L^{-1}$) decreases the proton conductivity [18].

3.2. Effect of molecular weight

Asensio et al. [24] reported that molecular weight (MW) has a vital role in improving mechanical strength. In order to prepare a highly conductive membrane, the polymer matrix with a comparably higher molecular weight should be applied. However, such an approach may not have a significant impact on the resulting proton conductivity of PEMs.

3.3. Polymer composites

An effective approach to improve the proton conductivity of PEMs is to incorporate some additional components. Composite membranes showed promising potential to be used as HT-PEMFCs. Composite materials consist of two or more constituents with different chemical, mechanical, or physical properties [25]. Composite membranes have widely been used in PEMFCs such as PTFE/Nafion [25], metal-oxide-recast/Nafion [26], copper phthalocyanine tetrasulfonic acid tetrasodium salt (CuTSPc)/Nafion [27], calcium titanate/PBI [28], PBI/graphene oxide [29], etc. The change in H_2 crossover and proton conductivity at different operating conditions with/without filler in Nafion is illustrated in Figure 1. As shown in Figure 1(a), the channels within the membrane are fully saturated with water and the mechanisms for proton conduction can be either “Grotthus” or diffusion. In this case, open circuit voltage (OCV) can be reduced due to the molecular H_2 passing through the membrane (H_2 crossover). At higher temperatures (Figure 1(b)), water begins evaporation and results in the shrinkage of the channels and decreasing proton conductivity. On the other hand, H_2 crossover improves at elevated temperatures. Adding filler to the composite (Figure 1(c)) can decrease H_2 crossover and increase H_2 path to migrate from anode to cathode .[25]

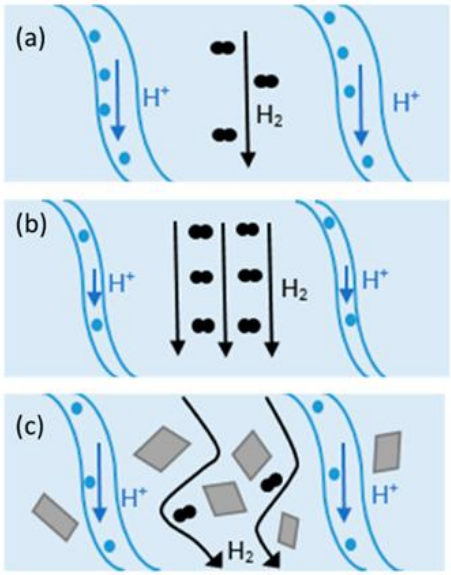

Figure 1 Proton and H_2 transport at (a) 80 °C, (b) at elevated temperatures, and (c) in Nafion composite at high temperatures [25]

Mixed-matrix membranes (MMMs) are a class of membranes comprised of a solid phase uniformly distributed in a polymer matrix. MMMs benefit from the advantages of the polymer membrane (high flexibility and ion exchange capacity) and inorganic constituents (high thermal and mechanical properties, water uptake, and proton conductivity) [30]. Among the inorganic materials, metal-organic frameworks such as Fe, Cr, Al, and Zr have high specific surface areas and offer higher proton conductivity. These MOFs can improve proton conductivity by defect engineering, post-synthetic modification, and impregnation with acidic molecules [31].

4. Proton conduction mechanism

Numerous reports have been studied the proton conduction mechanism in PEM fuel cells; however, the exact mechanism of proton conduction in the PEMs has not been fully recognised and understood yet. Among various theories introduced so far, the ‘Vehicular’ and ‘Grotthuss’ mechanisms have been more commonly approved to explain the proton transfer mechanisms in PEMs [32][33]. Usually, the PEMS with activation energy below 14 KJ.mol^{-1} can be explained better with the ‘Vehicular’ mechanism, while those exhibit higher activation energies are better represented with the ‘Grotthus’ mechanism [34]. In fact, the proton transfer explained by both the ‘Vehicular’ and Grotthus mechanisms does not act independently in PEMs. Both theories can make helpful assistances to understand better the proton conduction mechanism in PEMs. The proton transfer happens with a ‘vehicle’ or proton solvent (for example, water molecules as hydrates in the PEM molecular structure) with providing a suitable diffusion rate in the ‘Vehicular’ mechanism [35]. In the ‘Grotthuss’ mechanism known as the ‘hopping’ mechanism, a vehicle or proton solvent is not essential. Protons could simply jump from one site to another alongside the proton acceptor sites in the PEMs backbone [36]. Figure 2 displays a schematic diagram illustrating both the ‘Vehicular’ and ‘hopping’ mechanisms for proton conduction paths in PEMs.

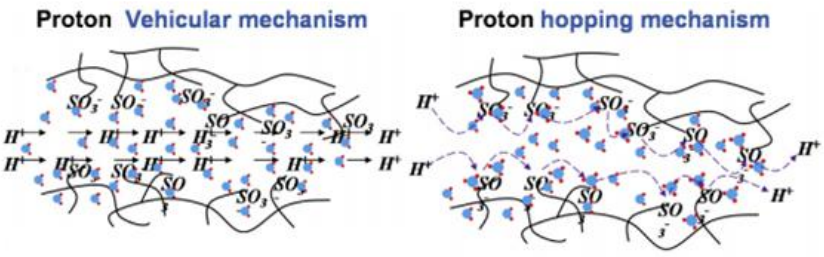

Figure 2 The Schematic design of the Vehicular Mechanism and hopping mechanism as proton conduction in PEMs [37] [38].

5. Degradation and fuel cell performance

The degradation of the PA-doped PBI-based membrane can be initiated by the chemical degradation, which happens by H containing end-groups attacked with hydrogen peroxide and its radicals that finally results in a mechanical/thermal degradation [39]. The N-H bond attack in the imidazole ring causes a ring-opening for imidazole and ‘scission’ of the macromolecular chain, which can be studied by FTIR spectra. In the PA-doped PBI membranes, the PA has an inhibiting effect on the decomposition of H_2O_2 and hence can decrease the chemical degradation of the PBI membrane [39]. A research study in this field has reported that the PBI membrane displayed 15% weight loss after 20 h of exposure to a 3% H_2O_2, which was higher than that of the Nafion 117 membrane [40]. In another study, the stress at the break of the PBI membrane dropped from 52.9 MPa to 33.9 MPa due to the peroxide attack [41]. The physical properties can be considered as an essential factor in the degradation of the PEMs. Deformation of the membrane, which takes place due to the compressive forces of the bipolar plates in MEAs, leads to pinhole formation and can decline the chemical degradation of the PEMs [42]. The swelling and shrinking of the PBI membrane can cause mechanical stress to the membrane. From thermal stability results, there is no significant weight loss at 150 °C and 500 °C [43][44].

6. Experimental characterization

6.1. In-situ characterisation

The polarization curve named the I – V curve can be measured by less expensive electrochemical devices and methods. The method can be done using a potentiostat-galvanostat analyser over a range of temperatures and hydrogen/oxygen flow rates [45]. The impedance spectroscopy and cyclic voltammetry are known as more expensive methods compared with the polarization curve [46][47]. In this method, the electrical current is changed, and the equivalent voltage output is measured and plotted against the current density. The voltage output is an important parameter as well that shows the figure of merit for a fuel cell [48].

6.2. Ex-situ characterisation

Ex-situ characterization techniques can be used in complementarity with in-situ electrochemical techniques. These techniques significantly affect PEM fuel cells' progress, particularly to understand the morphology of their component and stability [49][50]. The Raman spectroscopy, infrared (IR), and nuclear magnetic resonance (NMR) spectra have been used to explore the PEMs and their protonation by different acids [29][39].

6.3. In-plane and through-plane techniques

In-plane conductivity measurement is a technique in which two platinum plate electrodes and a sheet of the sample (membrane) are mounted on a Teflon cell, and two parallel Pt electrodes are placed on one side of the membrane. To measure the proton conductivity in liquid water or at relative humidity lower than 100%, the cell is placed in a distilled deionized water or a humid chamber with controlled humidity (thermos-controlled humid chamber), respectively [51].

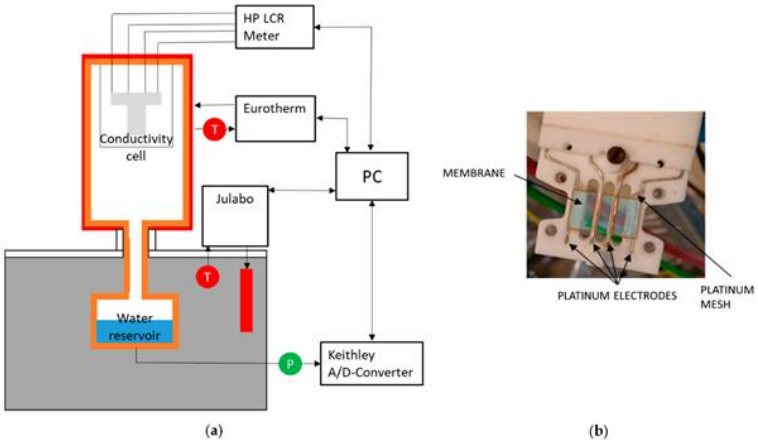

Figure 3 Schematic of in-plane test set-up [52].

Another technique for measuring the proton conduction is *through-plane* conductivity. The test set-up is comprised of two PTFE blocks that build the framework and the membrane sheet is placed between two Pt electrodes. To determine the resistance, the high-frequency intercept of the impedance with the real axis should be used [52][51].

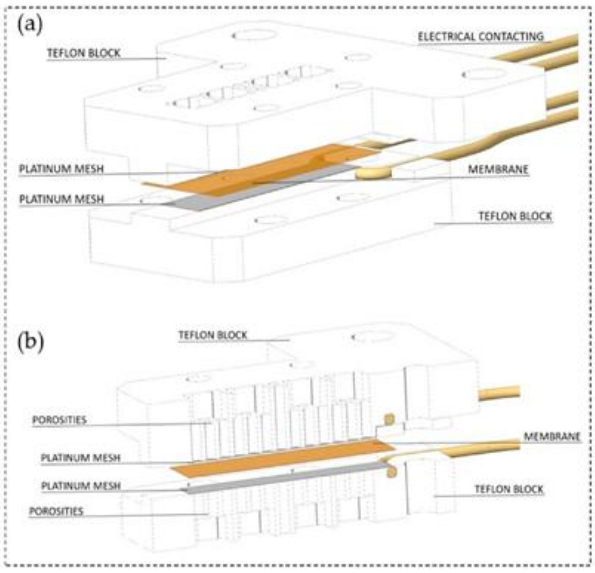

Figure 4 Schematic of through-plane test set-up [52]

6.4. The 2-probe electrodes and 4-probe electrodes cells

In terms of the functional probe configuration, the EIS measurement can be classified into two major groups: 2-probe and 4-probe configurations [53]. In the 2-probe configuration, the electrodes operate under low frequencies and an alternating electric field. Before polarity reversal, some ions may reach the electrodes, and thereby the electric field in the membrane decreases (electrode blocking) [54]. In the 4-probe configuration, the charge build-up effect near the electrodes diminishes because of using different electrodes with sufficient distance from the charge build-up region. The distance between the probes in both configurations plays an important in measuring the conductivity [55]. It has been reported that the 2-probe configuration can be used for high-resistance materials because of the negligible impedance in the circuit. On the other hand, the 4-probe arrangement is the appropriate choice for the ionic conducting materials with low resistivity due to the diminished interfacial effects in these materials [55].

A summary of the different possible configurations (geometry and analysis techniques) for the EIS measurements is shown in Figure 5.

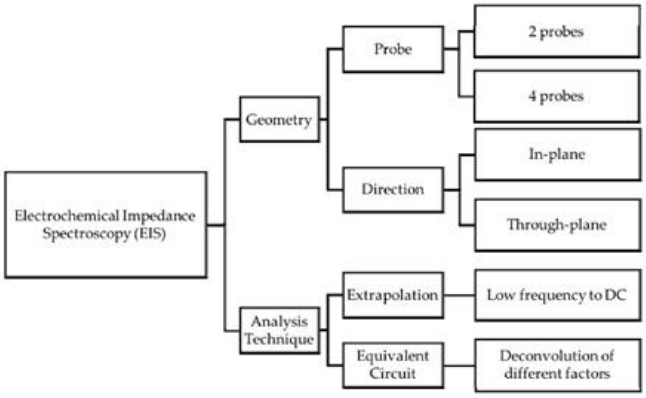

Figure 5 Possible configurations for EIS measurement [55].

6.5. Proton conductivity and PA doping level

The proton conductivity of PA-doped PBI membranes has been studied by several researchers. The researchers measured the anhydrous proton conductivity of different PA-doped PBI-based PEMs and proposed that the conductivity mechanism is dominated by the proton transfer from an -N site to a neighbouring vacant one by the phosphate counter-ion through a Grotthus mechanism. They confirmed counter-ion mobility by 1H and 31P NMR analysis [56]. The bound- and unbound-PA molecules and $H_2PO_4^-$ anion in PA-doped PBI-based membranes mainly participate in the proton conduction through the 'Grotthus' mechanism [57]. Generally, the PA doping level (PA_{dop}) has been achieved by dipping the membranes into PA (85 wt.%) for five days [57]. In this method, the membranes were dried in a vacuum oven at 60 °C for 24 h, and the doping level was determined by measuring the absorbed acid weight by the membranes [58].

6.6. Thermal, chemical, and mechanical stability

The Fenton test has been widely used to study the chemical degradation of PBI-based PEMs [118]. The chemical stability of PEMs is of much concern to the lifetime of PEM fuel cells. In the Fenton test, ferrous ions (Fe^{2+}/Fe^{3+}) were used as the catalyst for H_2O_2 decomposition. The chemical stability of the PBI membrane (weight loss) was measured in H_2O_2 solutions having a trace amount of ferrous ions (Fe^{2+}/Fe^{3+}) [39]. The •OH or •OOH radicals form in situ from the decomposition of H_2O_2 and attack the polymer chain that has hydrogen bonding. The PEMs based on perfluorinated sulphonic acid such as Nafion display high chemical stability than those based on polyaromatic hydrocarbons [40].

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