Enhanced Proton Conductivity of Porous UHMWPE membrane with Graphene-based material for Vanadium Redox Flow Battery

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Abstract. Porous membrane with enhanced proton conductivity is designed and prepared for vanadium redox flow battery (VRFB). The membrane is composed of ultra high molecular weight polyethylene (UHMWPE) grafted with poly(vinylbenzyl chloride) (PVBC) at different degrees of grafting (DOG). Subsequently, the membrane is functionalized with graphene oxide (UHMWPE-g-PVBGO) under ultrasonication. The functionalization of the GO on the porous substrates is confirmed by Fourier transform infrared (FTIR) and Raman analyses. UHMWPE-g-PVBGO membranes exhibited ~37% higher proton conductivity compared to pristine UHMWPE upon modification at 30 °C and 100% relative humidity (RH). In relation to the degree of grafting, a higher degree of grafting possessed higher proton conductivity value for the porous membrane.

1. Introduction
The rapid progress of vanadium redox flow battery (VRFB) as one of the most promising electrochemical energy storage has influenced vigorous research on technology improvement. Comparing VRFB to other flow batteries, VRFB offers longer life cycle, flexible design, deep discharge capacity and low environmental risks [1]. In VRFB, the membrane plays a vital role in determining the potential commercialization and performance of the system. A membrane separates the positive and negative electrolytes while providing the diffusion of balancing ions such as protons (H+) to complete the circuit [2]. Although VRFB has been successfully applied in various application fields, the expensive cost of the membrane hinders the commercial development of the battery system. In addition to this, rigorous research is also currently underway to further improve the performance system. Practically, an ideal membrane for VRFB should have high proton conductivity to avoid the ohmic losses, low vanadium permeability to prevent high self-discharge, excellent chemical and mechanical stability in the acidic and oxidative environment of the electrolytes and low cost for easy commercialization [3, 4].

Porous polyethylene (PE) is a porous membrane that has been used in many battery applications especially for lithium-ion batteries (LIB) [5, 6] and fuel cell [7, 8]. The use of PE in such applications can be regarded as versatile and promising due to its ability to withstand high temperatures and possessed superior chemical and mechanical stability. Additionally, the cost of these materials can be
obtained as low as $5–50 \text{ m}^{-2}$ [9, 10]. The potential use of PE for VRFB has been discovered in many studies. A study conducted by Jung et al. (2018) proved that the stability of the PE membrane is 27 times higher than Nafion with comparable performance in VRFB [11]. The excellent stability of such membrane against the vanadium electrolytes is due to its poor wettability [12]. Although this membrane is chemically stable, the high hydrophobicity of such membrane leads to a severe reduction in the proton conduction and simultaneously reduce the battery efficiency.

Generally, most porous membranes are hydrophobic; hence the proton conductivity of such membrane material is low ($\sim 10^{-12} \text{ S cm}^{-1}$) [13]. This is because, in the porous membrane, the hydrophilic functionalities like sulfonic acid, carboxylic acids, and quaternary ammonium pendants do not exist in the membrane structure. Hence, hydrophilic materials are required to make the membrane structure to be compatible with the water and to achieve excellent electrochemical properties in the VRFB. There have been extensive studies in improving the properties of the porous membranes. One of the most effective ways to enhancing the conductivity is by modifying the membranes with hydrophilic materials such as silica [14, 15], TiO$_2$ [16] and zeolite [17].

Graphene oxide (GO) is a carbon-based material that has plenty of functional groups, making this material to be readily surface modified with other materials. In an attempt to improve the proton conductivity of porous membranes for specific applications, GO served as one of the best choices. A study conducted by Karim et al. showed that GO ($10^{-2} \text{ S.cm}^{-1}$) has higher conductivity compared to graphite oxide ($10^{-4} \text{ S.m}^{-1}$) and graphene oxide/proton hybrid ($10^{-5} \text{ S.cm}^{-1}$) [18]. The existence of many oxygenated-functional groups on the GO surface makes GO to exist as negatively charged, hence promoting the transportation of the positively charged $\text{H}^+$ through the hydrogen bonding network. Hence, combining this feature with the porous membrane would help to alleviate the low proton conductivity in the membrane.

In this paper, a commercial Ultra-Height Molecular Weight Polyethylene (UHMWPE) was used to fabricate high proton conductivity membranes. The UHMWPE was activated with polyvinyl benzene (PVBC) to provide an active site for the interaction with GO. The establishment of the modification technique was verified by using the chemical and morphological analyses to identify the presence of the GO on the membrane surface. Furthermore, the proton conductivity value of the pristine and modified membranes was measured and compared through electrical impedance analysis. The results demonstrated enhanced proton conductivity with lower area resistance for the developed membranes.

### 2. Methodology

#### 2.1. GO Functionalisation

Few different surface-modified composite membranes were prepared in this research. To introduce the functional site for the UHMWPE, the porous substrates were first activated by poly(vinyl benzyl chloride) (PVBC) of different degree of grafting (DOG) by using the following procedure [19, 20]. Electron beam accelerator (EPS 3000) was used to irradiate the samples. The degree of grafting was calculated using the following equation:

$$\text{DOG} (\%) = \frac{W_g - W_s}{W_s} \times 100$$

Briefly, the activated UHMWPE is immersed in 3.0 wt% of GO under sonication for 24 hours. The samples were then washed for 5 times with deionised water to removes the weakly bonded GO. Subsequently, the prepared samples were vacuum-dried overnight at 60°C. The membranes were denoted as UHMWPE-g-PVBGO (x%) where x represents the DOG. Figure 1 shows the schematic representation of the membrane preparation steps.
2.2. Characterisation and Analysis
The analyses of the chemical and morphological surface of the prepared membranes were investigated. The infrared (IR) absorption was recorded in the region of 6000 – 400 cm\(^{-1}\) by using FTIR spectrophotometer (Perkin Elmer, USA). Raman spectroscopy was also carried out to complement the IR analysis on the presence of the GO on the membrane surface.

2.3. Proton Conductivity Measurement
The conductivity of the membranes was measured before and after modification. Electrochemical impedance spectroscopy (EIS) was used to record the conductivity and the area resistance of the membrane from ZPlot software. Before the measurement, the membranes were equilibrated with the acid solution overnight. The conductivity value obtained for all samples were measured at 100% relative humidity at 30°C. Equation 3 shows the formula used in calculating the conductivity and area resistance of the membranes:

\[
\sigma \left( \text{S cm}^{-1} \right) = \frac{L \text{(cm)}}{R \Omega \times S \text{(cm}^2)}
\]

Where \(L\) is the membrane thickness, \(R\) is the resistance and \(S\) is the membrane active surface area. The denominator of this equation can also serve as the area resistance of the membrane.

3. Results and Discussion
Few types of porous membranes with different DOG were obtained by surface modification with GO layer. Figure 2 shows the schematic representation of the chemical interaction of the activated porous substrates with GO at the surface. Three prominent peaks are obtained from the FTIR analysis which corresponds to \(-\text{CH}_2\) (symmetric and asymmetric stretching at 2849 cm\(^{-1}\) and 2916 cm\(^{-1}\) respectively) and \(-\text{CH}_2\) deformation (1463 cm\(^{-1}\)). The traces of GO on the membrane surface can be seen on the additional peaks of oxygen-containing groups shown by the modified membranes. The vibration of C-O stretching of \(-\text{COOH}\) appeared at around 1250 cm\(^{-1}\). The bands that can be observed at 1050 cm\(^{-1}\) corresponds to the stretching vibration of epoxy group (C-O-C). The peak at 1727 cm\(^{-1}\) represents the C=O stretching [21].
To further confirm the GO functionalization procedure, Raman analysis was carried out. Figure 3 shows the Raman analysis of the pristine and modified membranes. Comparing the pristine and modified membrane, the modified membrane shows fundamental peaks in 1250 to 1750 cm$^{-1}$ region. The peak at 1353 cm$^{-1}$ can be associated with the D vibration band caused by the disordered structure of GO. Meanwhile, the G vibration band at 1587 cm$^{-1}$ correspond to sp$^2$ carbon atoms plane stretching motion. In addition, the peak intensity of the modified membrane at around 2500 – 3000 cm$^{-1}$ regions become widen as the result of the interaction between GO and the grafted substrates [22].

Proton conductivity is important parameter that directly affect the voltage efficiency (VE) of a VRFB system. For porous substrates, usually the proton conductivity is very small (~10$^{-12}$ mS cm$^{-2}$) since there is no ion exchange that can serve as the ion exchange site to carry the H$^+$ ions. Hence, the conductivity value of the porous membranes depends on the size and pore exclusion effect of the porous membrane. In addition to the low proton conductivity, porous membrane also highly hydrophobic in nature with low wettability to carry the water transport through the membranes.

Table 1 shows the proton conductivity and area resistance of the membranes. Upon modification with GO under sonication, the membrane surface is covered with layers of GO. The proton conductivity
of the modified membranes was found to be higher than the pristine membrane. At higher DOG, the proton conductivity increase. This DOG represents the amount of available site for OH from the GO to be interconnected with CH₂-Cl bond through the normal covalent bond [18]. As the results, the negatively charged GO form hydrogen bond with the water molecule to facilitate faster proton transportation through the porous structure of the membrane. Area resistance of the modified membranes showed a reverse trend since more protons can move freely through the membrane. Table 1 shows the proton transfer through the modified membranes.

### Table 1. Proton conductivity and area resistance of the membranes

| Membranes                      | Thickness (mm) | Conductivity (mS cm⁻¹) | Area Resistance (Ω cm²) |
|-------------------------------|----------------|------------------------|-------------------------|
| Pristine UHMPWE               | 0.07           | 27.4                   | 0.255                   |
| UHMWPPE-₇-PVBOGO (10.5%)      | 0.07           | 30.44                  | 0.230                   |
| UHMWPPE-₇-PVBOGO (11.7%)      | 0.07           | 30.61                  | 0.229                   |
| UHMWPPE-₇-PVBOGO (25.1%)      | 0.08           | 37.71                  | 0.212                   |

**Figure 4.** The proton transfer through the modified membranes

### 4. Conclusion

The modification of UHMWPE membrane was successfully carried out using GO to enhance the proton conductivity of the membrane. FTIR and Raman analyses was carried out for both pristine and modified membrane to confirm the presence of GO on the membrane surface. The proton conductivity value of the membrane increased with the increased in the DOG. The GO on the membrane surface increases the ionic functionalities of the porous membrane. Hence, resulting in an increase in the proton conductivity value.

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