

Preparation of porous membrane with graphene oxide for vanadium redox flow battery

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Abstract. Graphene oxide (GO) was functionalized onto both sides of grafted porous polyethylene/polypropylene (PEPP) membrane sheet through sonication and simple immersion. Graphene oxide is a trending material in the field due to its excellent properties such as highly resistant to alkaline/acidic and strong mechanical strength, low cost and easily accessible. PEPP was successfully modified and the fiber gap of PEPP was reduced by grafting with GMA functionalized with GO. With addition of GO, modified PEPP membrane became hydrophilic with the addition of hydrogen bond from the GO. The FTIR results also showed traces of GMA on the surface of PEPP and after functionalized the membrane, it has shown prominent new peak which correspond to the C bond from GO from ultrasonication method.

1. Introduction

1.1. Vanadium Redox Flow Battery

Vanadium redox flow battery (VRFB) has attracted significant attention for its great potential as electrochemical energy storage (EES) due to its scalability and versatility in comparison to other redox flow battery options such as Zinc-Bromide or Iron-Chromium. Other properties of VRFB are low electrolytes contamination as VRFB uses all vanadium states (V^{2+} , V^{3+} , V^{4+} , and V^{5+}) in both positive and negative electrolytes, good electrochemical reversibility, great performance and long life cycle [1–4]. VRFB typically consists of set containers for electrolytes, a pump and a single cell unit as its basic setups.

The main piece of VRFB is the membrane as the membrane acts as a divider to inhibit cross-mixing of electrolytes from both sides as well as to complete the circuit as it allows ion transfer from anode to cathode [5–6]. An ideal characteristics look for VRFB are low vanadium permeability, high mechanical and chemical stability, high ion conductivity and low cost [7–9]. The favorable choice of membrane used in VRFB is the Dupont Nafion series including N115, N117, N112, N1135 as well as N1100 which is preferred for their high proton conductivity at an average of 100 mS cm⁻¹ and high mechanical strength and chemical stability. Even though Nafion is commercially used for VRFB, it had a significant setback as it has high vanadium permeability which causes a drop in the performance of



VRFB and also low ion selectivity [2,7,10,11]. Nafion membrane cost also a concern to be considered as it is highly expensive costing around \$500 to \$1000 per m² [2,12,13].

1.2. Porous Membrane

Porous membrane has been in the spotlight as an alternative to replace Nafion. The porous membrane is a non-ionic membrane which has many potentials such as high stability, low costs and good proton conductivity [7,13,14]. However pristine porous membrane has been found to have high vanadium permeability despite its plenty advantages; thus further modifications are needed. Surface modification is a well-known method that can be divided into two, surface grafting and surface coating. Surface coating involved deposition of a thin layer onto the membrane surface however, it is unstable and the coated layers can be washed away during washing or while in an application. This is mostly due to the weak physical adsorption bond between coated layers and the membrane. Surface grafting does not face this problem by totally inserted the monomers onto the surface of the membrane by covalent bonding interaction.

Grafting polymerization for chemical modification and various techniques can be used such as UV photo-irradiation, plasma and high energy irradiation that can also cause recovery in water flux and hydrophilicity of the membrane [15]. However, UV irradiation have disadvantages such as poor penetration ability compared to gamma rays. The plasma method also has drawbacks as the chemical and physical alteration can only occur on the surface of the membrane. The best method to modify the surface of a membrane is by radiation-induced graft polymerization and has advantages such as homogenous reaction, no chemical inhibitors, high penetration rate and low amount of monomers needed to modify a membrane surface [15]. Previous studies reported even with grafting, the porous membrane is still unable to surpass Nafion. Thus, extra work required to make a porous membrane to meet the ideal criteria for VRFB application.

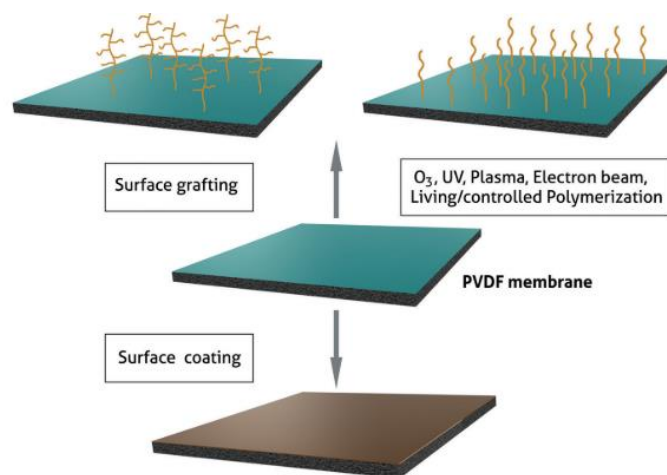


Figure 1. Route of surface modification of surface grafting and surface coating for porous membrane according to previous studies. [16]

1.3. Graphene Oxide

Carbon-based materials such as graphene and graphene oxide (GO)-based membrane have garnered a huge interest as substitute materials for VRFB applications in recent years. The versatile potentials for various applications such as separations and purifications, high selectivity for both gasses and liquids and antifouling are one of the attractions of GO-based membrane. Other properties of GO that attract researchers are strong mechanical strength, easily accessible, high resistance to strong acids/alkaline and organic solvents and low cost [17–19]. The potentials of GO are similar to the ideal characteristic properties for the VRFB membrane. The integration of GO with other types of nanomaterials will

increase the potential of GO and making it an excellent potential for conversion and energy storage devices [20]. Past studies indicated the addition of GO is helping to reduce the permeability issues of porous membranes as the hydrophilicity of porous membrane increased with the formation of hydrogen bonds on the surface of the membrane [19].

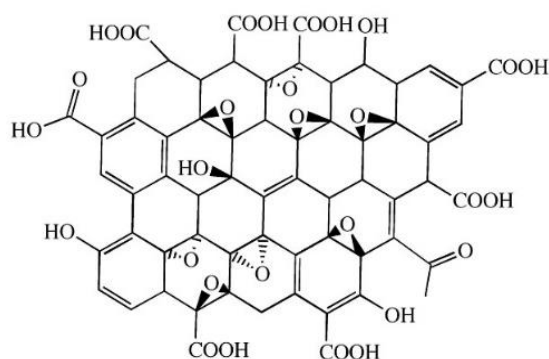


Figure 2. Molecular structure of Graphene Oxide.

In this study, pristine porous membrane polyethylene/polypropylene (PEPP) is modified using surface grafting with glycidyl methacrylate (GMA) and functionalized with graphene oxide (GO). The morphology and microstructure of the membrane were characterized by Scanning Electron Microscope (SEM) and Fourier-transform infrared (FTIR) spectroscopy.

2. Experimental

2.1. Material

Graphene oxide with monolayer content of 95% purchased from Graphenea, USA. Grafted PEPP with GMA was received from Nuclear Malaysia with degree of grafting of 180°. All reagent and membrane were used as received without further purification or treatment.

2.2. Characterization

The composite membranes SEM images were attained using the Philips XL30 field emission scanning electron microscope (FESEM) after coating with 5 nm Au. Fourier transform-infrared (FTIR) was executed using Agilent Cary 660 spectrometer.

2.3. Grafting

In the preparation of PEPP-g-GMA, all irradiation grafting will be done by Nuclear Malaysia Agency and the PEPP-g-GMA will be used as received. The reaction was performed following past work published somewhere else [21,22]. Usually, the PEPP membrane was placed in a polyethylene (PE) zip lock bags which were purged using purified nitrogen gas, sealed and irradiated using an electron beam accelerator (EPS 3000) to a total dose of 50 kGy, 100 kGy, and 300 kGy. Degree of grafting (dg) was determined by gravimetric method from the following equation:

$$d_g(\%) = \frac{W_g - W_s}{W_s} \times 100 \quad (1)$$

Where W_s and W_g are the weights of the original substrate and final grafted samples, respectively.

2.4. Functionalizing membrane

The PEPP-g-GMA will be functionalized with 5.0 % GO using sonication and a simple immersion method to determine which method is better. In both methods, PEPP-g-GMA will be functionalized for

24hr to ensure complete functionalization. In simple immersion, grafted PEPP was immersed inside a 25ml vials with 5.0 % GO solution. The vial was then secured using a retort stand and put inside a water bath with silicon oil and placed on top of a heating plate. Temperature estimated around 60°C was applied. Even though no heat was applied in the ultrasonication process, the temperature still rises and to ensure the same condition on both methods, the heat was applied to the simple immersion method. Similar to simple immersion, grafted PEPP was placed inside a 25ml vial with a 5.0 % GO solution as well for sonication. The vial was then put in a 50ml beaker filled with water before placed inside an ultrasonicator and left for 24hours with no heat applied. After 24h hours, both membranes were washed with deionized water for 5.0 hours to remove any excess GO and dried in an oven overnight.

3. Results and Discussion

3.1. Microscopy analysis of PEPP-g-GMA and proton conductivity

Images from Figure 3 showing a morphology of pristine PEPP membrane (a) and modified PEPP membrane (b). It is clearly observable in (b) modified PEPP has changed with its morphology compared to as it pristine state in (a). The structure of PEPP has been altered and thicker than it was before which reduces the gap between one fibres to another. The pore size of pristine PEPP has been reduced and thus help to reduce the high vanadium permeability of pristine PEPP. High vanadium permeability will cause the battery to self-discharge and results in low coulombic efficiency of VRFB. With reduced pore size, lower vanadium permeability was expected but this will impact low proton transfer as well. The role of graphene oxide was to promote the proton transfer to ensure modified PEPP will still have a good proton conductivity. Upon functionalization of GO, PEPP membrane change its hydrophilicity to a hydrophilic membrane from the hydrogen bond from GO. Hydrophilic properties of PEPP helps in boosting the proton transfer across PEPP membrane. Proton conductivity of modified PEPP was conducted under a temperature of 30°C and 100% relative humidity and was recorded to be 22.7 mS.cm⁻¹. **Figure** is an illustration of the mechanism of the functionalization of porous PEPP membranes with graphene oxide.

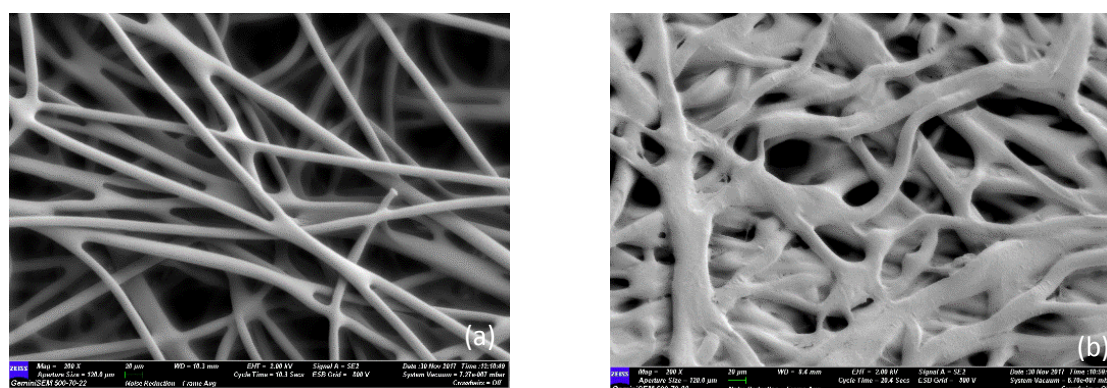


Figure 3. SEM images displaying morphology of pristine PEPP (a) and modified PEPP membrane (b).

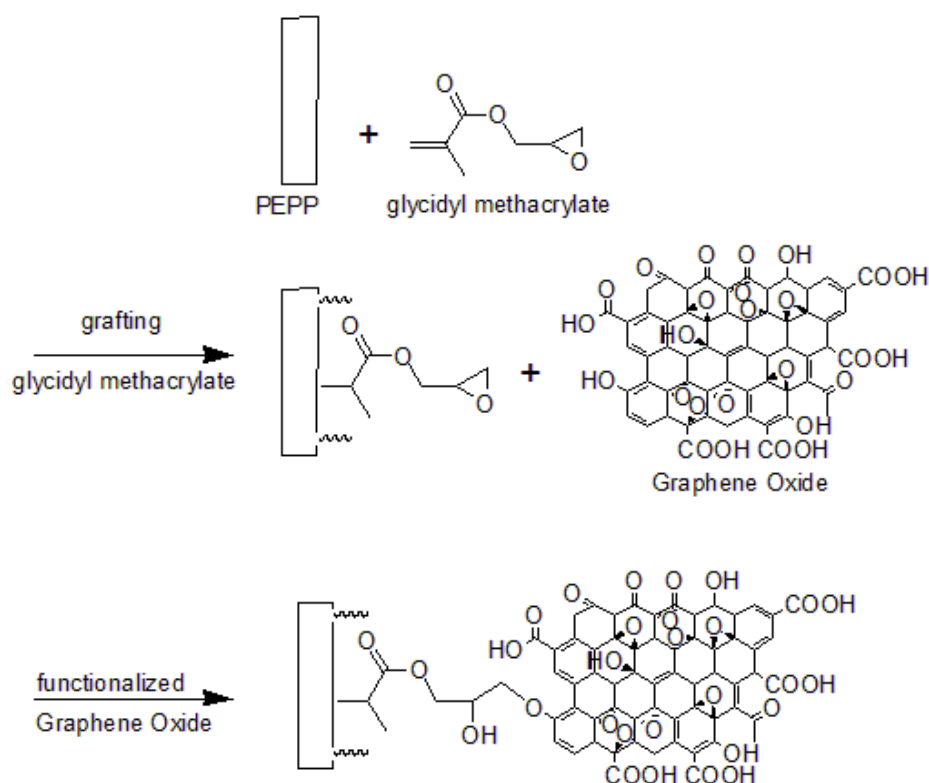


Figure 4. Mechanism of functionalization of porous PEPP membrane with graphene oxide.

3.2. FTIR analysis of PEPP-g-GMA and functionalized membrane

The IR spectrum of PEPP-g-GMA in **Figure** showed that there was a significant peak at 1724 cm^{-1} band which corresponds to the C=O bond from the structure of GMA. The peak around $3000\text{--}2950\text{ cm}^{-1}$ was the vibration of the CH_2 group. Upon functionalized with GO the peak around 1724 cm^{-1} for immersion reduced while sonication seems the same. A new peak also appeared around 1649 cm^{-1} at immersion and sonication indicated a sp^2 -hybridized C bond from the GO. The peak at 905 cm^{-1} was associated with epoxy of GMA however in immersion the peak seems reduced more than sonication. These peaks would indicate the reaction between GMA and GO, however, GO also had epoxy on its structure. Thus the slight reduction for sonication might indicate that the epoxy from GMA was reacted with GO but the signal was overlapped with its own epoxy reading while in immersion there was less reaction of GMA and GO. From this, we can conclude that the best technique for functionalizing GO between the two methods was ultrasonication. During the ultrasound process, the high-intensity ultrasound enables chemical reaction which functionalized GO with grafted PEPP membrane.

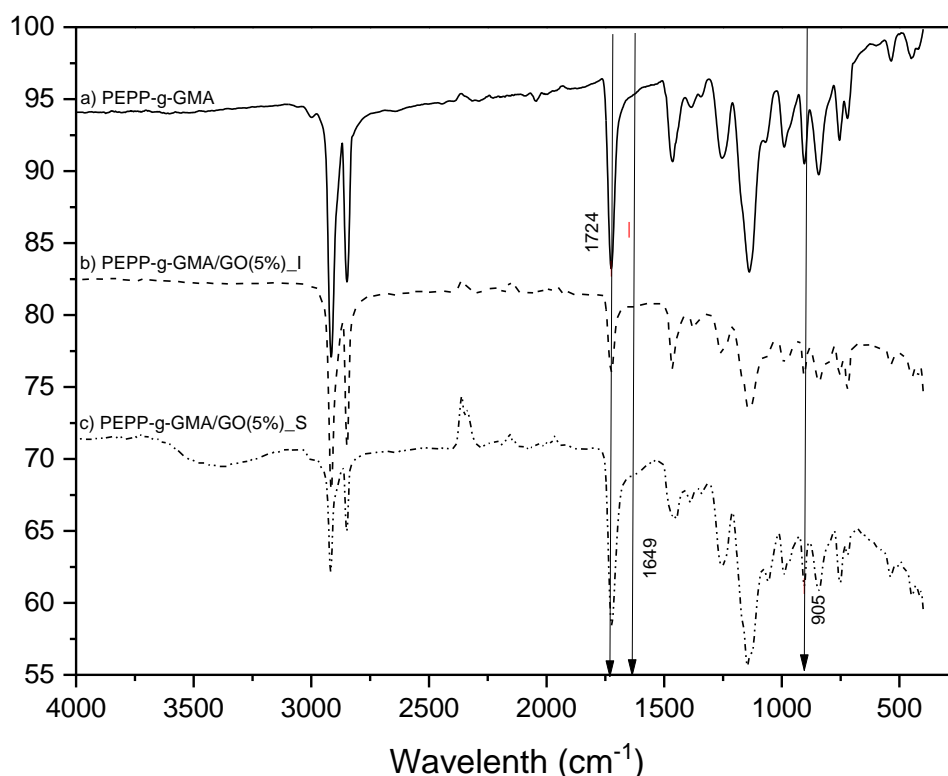


Figure 5. FTIR spectra of combined of PEPP-g-GMA (a) and functionalized PEPP-g-GMA with 5% GO content through simple immersion (b) and sonication (c).

4. Conclusion

The increasing of PEPP thickness showed that PEPP was successfully modified and thus reducing the porous size of PEPP. This will theoretically helps to reduce the vanadium permeability of the porous membrane. Further test is required to test the vanadium permeability of the modified PEPP. The FTIR results also showed traces of GMA on the surface of PEPP. After functionalized the membrane, it was found that sonication was the best method out of the two option as it has shown more prominent new peak at 1649 cm⁻¹ which correspond to the C bond from GO. The proton conductivity of the modified PEPP was recorded at 22.7 mS cm⁻¹. In compared with N117 which the commercial membrane for VRFB, proton conductivity of modified PEPP was lower by 69.9%. However, if compared with other modified porous membranes such as PES, modified PEPP has a similar value which was recorded to be around 22.4 mS cm⁻¹. The graphene oxide content may be varied and optimized in future work to find the best concentration to improve the performance of the modified membrane.

Acknowledgments

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5. References

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