

Surface modification of grafted porous polyvinylidene fluoride membrane with graphene oxide for vanadium redox flow battery

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Abstract. Vanadium Redox Flow Battery (VRFB) is an energy storage flow battery in which the key material for VRFB is the membrane that determines the cost and performance of the battery. Porous membranes have shown a great potential as a membrane due to their high stability, cheap and high selectivity. Poly(vinylidene fluoride) (PVDF) is a type of porous membrane that was extensively studied as a potential material for surface modification due to its thermal and chemical stability, inexpensive and mechanical properties. This study aims to develop a highly selective, high-performance modified PVDF membrane using surface grafting and functionalization for VRFB application using the sonication method. Graphene oxide (GO) is a trending material in the field due to its excellent properties such as being highly resistant to alkaline/acidic and strong mechanical strength, low cost and easily accessible. In this work, GO was functionalized on both sides of grafted PVDF using the sonication technique. Hydrogen bond from modification with GO caused the membrane to be a hydrophilic and FTIR results proved that new peaks appeared which relates to carbon bond from GO. Proton conductivity of modified membrane is recorded higher than commercial VRFB membrane, Nafion.

1. Introduction

Vanadium redox flow battery (VRFB) has been in the spotlight in research for its great potential as electrochemical energy storage (EES). These are owed to its large comparison to other redox flow batteries such as Iron-Chromium or Zinc- Bromide in terms of its scalability and versatility. Other than that, VRFB has low electrolytes contamination as such VRFB utilizes only vanadium ions but in different oxidation states. V^{2+} , V^{3+} , V^{4+} , and V^{5+} in both positive and negative electrolytes, respectively. On top of that, VRFB has a great battery performance, excellent electrochemical reversibility, and last but not least, a long life cycle [1–4]. VRFB's basic setup consists of a set of containers for electrolytes, a single cell unit and one or two pumps to circulate the electrolytes around.

The key component of VRFB is the membrane. The membrane in VRFB acts as a separator to prevent cross-mixing of electrolytes from both electrolyte sides as well as to complete the circuit as it permits ion transfer from anode to cathode [5-6]. Ideal criteria look in VRFB membrane are low vanadium



permeability, strong mechanical and chemical stability, high ion conductivity, and low cost [7–9]. The typical choices of VRFB membrane used are Nafion series from Dupont which are N115, N117, N112, N1135 and N1100 which are favored due to high proton conductivity which an average of 100mS cm^{-1} . Nafion also possesses strong mechanical strength and chemical stability to withstand the acidic condition of VRFB. Although Nafion is commonly used for VRFB, it has a major flaw that causes the drop in the coulombic efficiency of VRFB and also low ion selectivity which is its high vanadium permeability [2,7,10,11]. Other than that, the cost is also a concern to be considered as Nafion membrane is highly expensive costing approximately around $\$500$ to $\$1000$ per m^2 [2,12,13].

A promising alternative that has been in the spotlight to replace Nafion is the non-ionic porous membrane. It has many potentials such as low costs, high selectivity, and high stability which cover the ideal VRFB membrane characteristic [7,13,14]. However pristine porous membrane is flawed in one criterion which is high vanadium permeability, thus further modifications are needed to make it a good VRFB membrane. A well-known method that can be used is surface modification which is split into two categories, surface coating or grafting. Surface coating is a technique that involved the deposition of a thin layer of modifier onto the membrane surface. This technique is however unstable and leaching may occur during washing or while in an application due to the weak physical adsorption bond between coated layers and the membrane. This problem did not happen in surface grafting by completely embedding the monomers onto the surface of the membrane by covalent bonding interaction.

Various surface grafting techniques as illustrated in Figure 1 can be used to modify porous membranes such as UV photo-irradiation, plasma, and high energy irradiation. These modifications can cause recovery in water flux and hydrophilicity of the membrane [15]. Among these techniques, UV irradiation and plasma however have disadvantages. UV irradiation has poor penetration ability in comparison to gamma rays while in the plasma method, the chemical and physical alteration can only occur on the surface of the membrane. The best technique for this present work is to modify the porous membrane by radiation-induced graft polymerization. This technique has benefits as it has a homogenous reaction with no chemical inhibitors. It also possesses a high penetration rate and requires a low amount of monomers needed for the modification process [15].

However, as reported in previous work, even with grafting the porous membrane is still unable to surpass Nafion. Thus, extra processes are required to make a non-ionic porous membrane to become the ideal membrane for VRFB application.

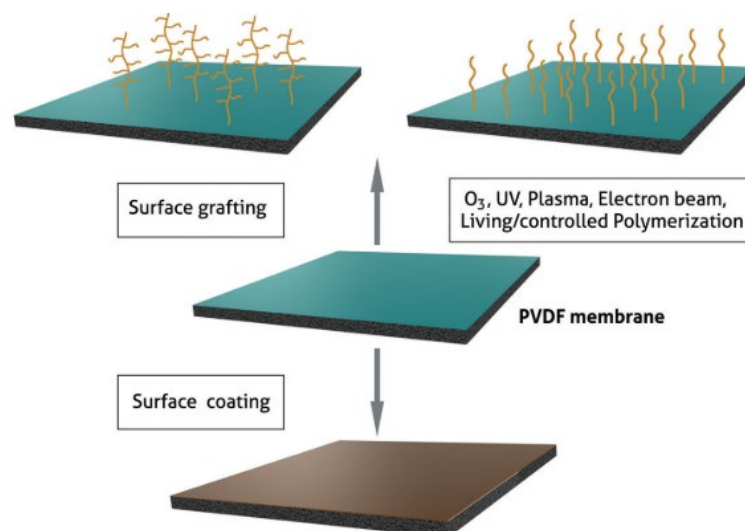


Figure 1. Path of surface modification of surface grafting and surface coating [16]

Graphene and graphene oxide (GO)-based membranes have brought in a huge interest as substitute materials for VRFB applications in recent years. Prospect for various applications which cover separations and purifications to a high selectivity for both gasses and liquids and also antifouling are one of the potentials of GO-based membrane. Other than that, GO possessed a strong mechanical strength and easily accessible materials which makes it a low-cost material. GO also have a strong resistance to acids/alkaline and organic solvents [17–19]. These characteristics of GO are similar to the ideal criteria of a VRFB membrane. The incorporation of GO with other nanomaterials will raise the probability of GO and make it an excellent prospective for conversion and energy storage devices [20]. Former studies directed that the incorporation of GO in membrane helps to reduce the permeability issues that porous membranes are facing by increasing the porous membrane hydrophilicity with the formation of hydrogen bonds on the surface of the membrane [19].

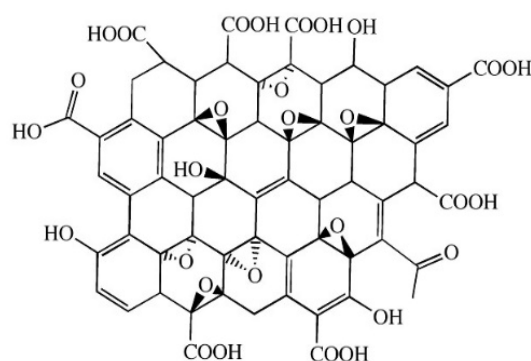


Figure 2. Molecular structure of Graphene Oxide

In this work, the surface of pristine porous membrane poly(vinylidene fluoride) (PVDF) is modified by grafting with vinylbenzyl chloride (VBC) and further, functionalized with graphene oxide (GO) on both sides to address the issue with Nafion and as an alternative membrane for VRFB.

2. Experimental

2.1 Grafting

In the preparation method for PVDF-g-PVBC, all irradiation grafting was done by Nuclear Malaysia Agency. The reaction was performed following procedure reported by Shin and Subashi [15,16]. Initially, PVDF membranes were placed in 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. The degree of grafting (d_g) was determined by the 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.

2.2 Functionalizing membrane

The PVDF-g-PVBC was functionalized with 5% GO using the sonication method. In the sonication method, PVDF-g-PVBC will be functionalized for two hours to ensure complete functionalization with no heating applied. The membrane was immersed in 5% GO in a sealed containers and place inside a

water bath beaker, before placed inside the sonicator. The sonicator will helps in breaking down the GO so that funtionalization between GO and membrane can toke place.

2.3 Characterization

Fourier-Transform Infrared Spectroscopy (FTIR) will be conducted using IRTracer-100 Shimadzu to observe the membrane IR spectra from 400 to 4000 cm^{-1} . Proton conductivity was tested using the 740 Membrane Test system, Scribner Associate, Inc.

The through-plane conductivity (σ in S/cm) is determined from the resistance of the membrane (R (Ω)), the thickness of the membrane (L (cm)) and the cross-sectional area which the current passes through (A (cm^2)) as noted in equation (2).

$$\sigma = \frac{L \text{ (cm)}}{R(\Omega) \times A \text{ (cm}^2)} = \frac{I L}{V A} \quad (2)$$

The first step in finding the membrane resistance, impedance spectra required to be analyzed to determine the high-frequency R_{HF} . ASR or uncorrected area-specific resistance ($ASR_{\text{uncorrected}}$ ($\Omega \text{ cm}^2$)) is defined by R_{HF} and the effective area ($A_{\text{effective}}$ (cm^2)) shown in equation (3).

$$ASR_{\text{uncorrected}}(T, RH) = R_{HF}(T, RH) \times A_{\text{effective}} \quad (3)$$

The accurate determination of the membrane ASR and conductivity requires correcting the as-measured ASR for the non-membrane ohmic resistances that contribute to the measured high-frequency resistance. The membrane ASR in $\Omega \text{ cm}^2$ is the difference between the as-measured, uncorrected ASR and the cell ASR.

$$ASR_{\text{membrane}}(T, RH) = ASR_{\text{uncorrected}}(T, RH) - ASR_{\text{cell}}(T, RH) \quad (4)$$

The through-plane conductivity of the membrane can be calculated using equation (5).

$$\sigma (T, RH) \left(\frac{\text{S}}{\text{cm}} \right) = \frac{L \text{ (cm)}}{ASR_{\text{membrane}} (T, RH)} \quad (5)$$

3. Results and Discussion

3.1 Image of PVDF-g-PVBC and PVDF-g-PVB/GO

Figure 3 show the images of the PVDF membrane before (a) and after modified (b) and (c) with VBC/GO. It is observable in (b) and (c) PVDF which was grafted and functionalized, changed its appearance compared to its pristine state (a). The surface of PVDF that has been modified with GO changed in colour, darker than it was before which indicated the GO was present on the surface of PVDF. The mechanism of the modified membrane from pristine to funtionalised membrane was illustrated in Figure 4.



Figure 3. Images of PVDF before and after modified with VBC and GO

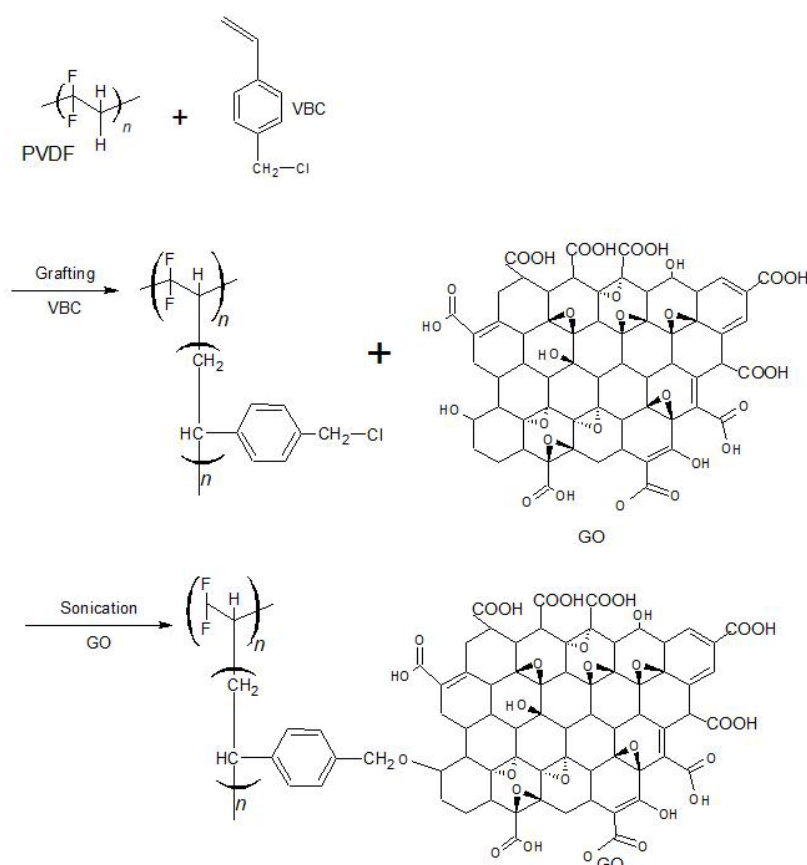


Figure 4. Mechanism of functionalization of porous PVDF membrane with graphene oxide

3.2 FTIR analysis of PVDF-g-PVBC and PVDF-g-PVB/GO

The IR spectrum of PVDF-g-PVBC in Figure 5 showed that there was a new peak around 1740 cm^{-1} band which correspond to C=O stretching of carboxylic acid group bond from the structure of GO. Upon functionalization with GO, the peak around 1516 cm^{-1} also slightly appeared due to C=C of graphite carbon bond. The new peaks appeared showed that GO was present in the modified PVDF membrane however the lack of intensity may indicate the insufficient functionalization of GO. This may be overcome by prolonging the time of sonication in the future longer than two hours to ensure a complete reaction between grafted PVDF and GO.

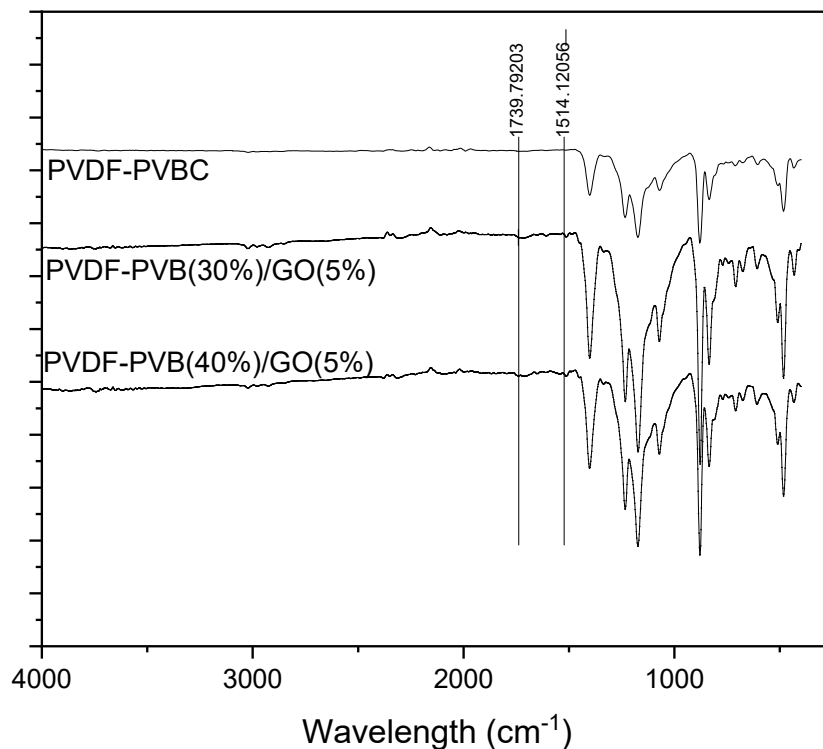


Figure 5. FTIR spectra of combined PVDF-g-PVBC and functionalized PVDF-g-PVB with 5% GO content at different degrees of grafting.

3.3 Proton Conductivity of PVDF-g-PVBC and PVDF-g-PVB/GO

The proton conductivity of the modified PVDF was recorded at 225 and 127 mS cm⁻¹ respectively for degrees of grafting 30% and 40%. In comparison to N117, the proton conductivity of modified PVDF was higher by 110% and 18%. These numbers showed that GO promoted the proton conductivity of the pristine porous membrane and details were listed in Table 1. The inconsistency in value however raised an issue that required attention as the lower degree of grafting 30% showed higher proton conductivity in comparison to 40%. More in-depth analysis and tests are required to further validate these values. In theory, the higher degree of grafting should possess higher proton conductivity. These values might not be illustrated properly because the grafted polymer was not homogenous and caused this inconsistency in the proton conductivity. In the future, repeated tests and average values might be done to avoid this irregularity.

Table 1. Details on Proton Conductivity of modified PVDF membrane and Nafion

Membrane	Thickness (μm)	Proton Conductivity (mS/cm)
N117	180	107
PVDF	110	70
PVDF-PVB(30%)/GO(5%)	120	225
PVDF-PVB(40%)/GO(5%)	120	127

4. Conclusion

The images showed that PVDF had been successfully incorporated with GO. This will theoretically help to reduce the vanadium permeability of the porous membrane. Further tests are required to test the vanadium permeability of the modified PVDF membrane using permeability diffusion cells. The FTIR results also showed traces of GO on the surface of PVDF. After functionalizing the membrane, it was found that a new peak at 1740 cm^{-1} and 1514 cm^{-1} correspond to the C bond from GO. The proton conductivity of the modified PVDF is higher than the Nafion membrane and pristine PVDF membrane. 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. Further work is also required in testing the character of the modified membrane and the performance of the modified membrane in a single-cell battery.

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