The sulfonation of polyvinyl chloride: Synthesis and characterization for proton conducting membrane applications

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ABSTRACT

Sulfonated poly-vinyl chloride (PVCs) membranes were synthesized first using an ethylenediamine solution to aminate the porous free-standing poly-vinyl chloride (PVC) membrane. This modified PVC was then reacted with sulfuric acid to form the PVCs material. The reaction time was varied to give PVCs materials of different degrees of sulfonation (DS). The membranes were characterized with FTIR and elemental analysis to confirm the presence of a $-SO_3H$ group. SEM was used to ensure the morphology had not changed during the reaction. Water-uptake and proton conductivity were measured and it was found that as the reaction time increased, both conductivity and water-uptake of the membranes increased compared to the unmodified PVC material. This study demonstrates a novel technique to impart increased water-uptake and proton conductivity to a PVC polymer without destroying the pre-existing membrane morphology.

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1. Introduction

Poly-Vinyl Chloride (PVC) is a very important polymer used in many applications, including the construction industry, biomedical applications [1], and as barriers or membranes. In particular, PVC based membranes are commercially employed as sensors for particular metals [2,3], as battery separators [4], and as proton exchange membranes (PEM) for fuel cell type devices [5]. For many of these different applications, the PVC must be modified in one form or another for desired functionality. In the case of proton exchange membrane fuel cells (PEMFCs), the PVC is generally modified to incorporate proton conductivity into the polymer.

PVC membranes have been used in fuel cell devices due to its excellent physical and chemical robustness, cost, and stiffness [6]. It is believed that H_2O_2 and its intermediates facilitate the degradation of membrane materials in fuel cell applications [7]. It has been generally well established that PVC materials are resistant to degradation by H_2O_2 [6], and therefore are excellent candidates for fuel cell based applications. For example, PVC materials are currently used in commercially available fuel cell-type sensors.

In a PEMFC, the PEM serves to physically and electronically separate the anode and cathode while enabling protons to rapidly traverse from the anode to the cathode [8]. If the conductivity of the PEM is poor, device performance tends to suffer [7,8].

The conductivity of a membrane is dependent on two main properties. First is the degree of sulfonation (DS) of a polymer or film. It is often more convenient to determine the ion exchange capacity (IEC) experimentally, which is directly related to DS. For many commercially available PEMs, a strong correlation between IEC/DS on proton conductivity has been observed [9–12]. Second, the conductivity of the PEM can depend greatly on its water content [8,11,12]. The hydrated polymer's conductivity can be mainly attributed to phenomena known as the "Grotthuss Mechanism" [13], in which protons can hop from bulk-type water retained within the pores of membrane. This mechanism contributes more significantly to the conductivity of a polymer than proton hopping between sulfonic acid groups. However, the hydrophilicity of the sulfonic acid groups is the main driver of water retention within the polymer. Thus, water content and IEC are often closely linked.

A PEMFC can come in different forms, including power generating devices as well as sensor devices like breath alcohol sensors (BrAS). While the performance of each form depends on both conductivity and water content of the membrane, the sensor-based PEMFCs reliance on conductivity is much lower than that of a power generating PEMFC. This is due to the fact that the currents generated in the sensor are far lower than those of a power generating cell [14,15]. However, sufficient water content is still extremely important for sensitivity in those devices. Water content in a membrane can often depend greatly on the relative humidity (RH) of the environment into which it is deployed. As such, ways to maintain membrane hydration are critical for reliable operation.

The PVC membranes commonly employed in commercial BrAS's are prepared from spherical PVC particles that have been

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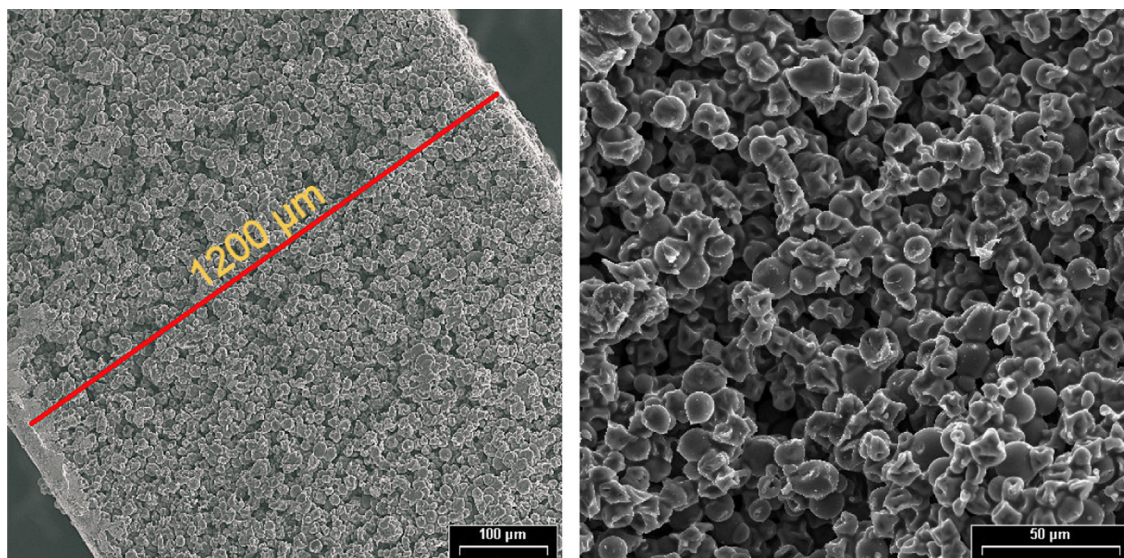 *E-mail address:* Brad.Easton@uoit.ca (E.B. Easton).

Fig. 1. Cross-sectional SEM (Left) and close up (Right) of porous PVC found in commercially available sensor PEMFCs.

compressed into a free standing film. Fig. 1 shows an SEM image of such a membrane composed of 10 μm PVC spheres. The PVC itself is a poor proton conductor. Thus, the void volume between the spheres is impregnated with sulfuric acid. Therefore, the PVC is essentially serving as a matrix to hold the electrolyte. However, over time this can be problematic in that the proton conductivity can drop by five orders of magnitude upon exposure to very low RH [15]. While proton conductivity can be restored upon rehydration, this may not be practical during field operation. Furthermore, dehydration/hydration cycling promotes the loss of electrolyte from membrane, leading to unrecoverable loss of conductivity and/or corrosion of device components. As such, it is highly desirable to enhance the water uptake and retention capabilities of PVC under dry conditions.

PVC-based materials can be modified to improve performance. For example, Fu et al. have modified PVC membranes with polystyrene sulfonated (PSS), forming PSS within the pores of the preformed PVC membrane [5]. Recently, Panawong et al. have dissolved PVC and chemically grafted polystyrene (PS) onto the backbone. While this did destroy any pre-existing PVC morphology, the recast composite membrane did show improved optical sensitivity for Fe^{3+} [16].

Here we have employed an approach to covalently modify the surface of the porous PVC to endow it with greater conductivity, while maintaining the existing porous morphology. To do this, we have employed a solvent system which will not dissolve the PVC membrane and performed covalent modification to the outer surface of the spheres, as shown in Fig. 2. Such an approach has been commonly employed for the modification of carbon surfaces to improve proton conductivity [17–22]. However, to the best of our knowledge, this is the first time such an approach has been used for PVC membranes. In this report, we have prepared a series of sulfonated PVC membranes (PVCs) with varying degrees of sulfonation and examined its influence on solvent retention and proton conductivity under low relative humidity at ambient temperature.

2. Experimental

2.1. Materials

Free standing PVC membranes were donated by Alcohol Countermeasure Systems (ACS) in 15 cm × 15 cm sheets with a thickness of 1.5 mm. The PVC used for experiments was cut to size as needed. The PVC was used as-received with preparatory work required. The PVC pressed spheres are approximately 10 μm in diameter with pore sizes of similar diameter. Ethylene diamine (EDA) (99%) and sulfuric acid (99%) were obtained from Sigma-Aldrich.

2.2. Preparation of PVCs

PVC was sulfonated by a two-step reaction as shown in Scheme 1. A 90% solution of EDA was heated to 80 °C. PVC was cut into 2 cm × 1 cm pieces and added to this solution and allowed to react for different time periods, ranging between 30 min and 24 h. After the desired period of time, the PVC was removed carefully, and allowed to stiffen before washing. The PVC was washed repeatedly with deionized water (DI) water to remove any excess EDA. After sufficient washing, the membranes changed from a cream white color to a range of orange to dark red, depending on the reaction time. The EDA treated PVC membranes (denoted hereafter as PVC-EDA) were then dried in a vacuum oven at 60 °C for 24 h. The membranes were removed from the oven and placed into 4 M sulfuric acid at room temperature for 24 h to complete the sulfonation reaction (denoted hereafter as PVCs). The membranes were removed from the 4 M sulfuric acid solution, washed with DI water and placed into DI water for storage prior to use.

2.3. TGA and IR analysis

Thermogravimetric analysis (TGA) was using a TA Instruments Q600 SDT thermal analyzer. Samples were dried in an oven under vacuum at 60 °C before testing. The samples were initially held at 80 °C for 15 min to ensure they were fully dried and the mass at this point was defined as the 100% value (the "dry mass") [23]. The analysis was performed under flowing argon with a heating rate of 20 °C/min from 80 °C to 1000 °C.

FT-IR was performed using a PerkinElmer Spectrum 100 instrument. The samples were also dried before use similar to the conditions described for TGA measurements. The analysis was performed using an attenuated total reflectance (ATR) germanium crystal with a scan between 4000 cm^{-1} and 700 cm^{-1} with a resolution of 2 cm^{-1} for 10 scans. The samples were pressed with a force between 30–50 N onto the ATR crystal.