

Poly(vinyl alcohol)/sulfosuccinic acid (PVA/SSA) as proton-conducting membranes for fuel cells: Effect of cross-linking and plasticizer addition

Jing Zhang, Gaopeng Jiang, Jingjing Shi,
Pan Xu., Jinli Qiao*

College of Environmental Science and Engineering,
Donghua University, 2999 Ren' min North Road,
Shanghai 201620, China
*qiaojl@dhu.edu.cn

The polymer electrolyte membrane fuel cell (PEMFC) have evoked considerable attention owing to its overcoming of corrosion problem. As a key component, the function of the polymer electrolyte membrane is a barrier to avoid the direct contact between fuel and oxidant and a proton conductive medium. However, its high cost and difficulty in synthesis and processing, such as Nafion[®] membrane, still limit the wide applications of this technology (1-4). Hence, the development of cheaper and easier prepared polymer electrolyte membranes is urgently needed.

Cross-linking is a highly versatile method to create and modify polymers, in particular, to limit the swelling, which renders the membrane to be thermodynamically compatible with water (5-6). On the other hand, the addition of plasticizer would assist the relaxation of the polymer chains through their special plasticizing effect. The special plasticizing effect will also influence the membrane stability which is also a key issue for a practical fuel cell usage. Based on this conception, we prepared a novel proton-conducting membrane composed of PVA and SSA to explore the effect of cross-linking and the plasticizer addition effect.

The membranes were prepared by a simple solution-casting method, where PVA (99% hydrolyzed, average molecular weight $M_w = 86,000-89,000$; Aldrich) was fully dissolved in water to make a 10% solution at 90°C. SSA (70% water solution, average $M_w=198 \text{ g mol}^{-1}$, Aldrich) and plasticizer, polyethylene glycol (PEG), were separately prepared and mixed to cast a membrane at ambient temperatures. Then the membranes were treated by thermal and chemical cross-linking procedures. Standing and flat membranes were obtained with a thickness about 40-70 μm . The effects of cross-linking procedure, cross-linking time and plasticizer composition on membrane proton conductivity are studied using AC impedance technique. TG analysis is used for membrane stability studies.

Figure 1 shows the proton conductivities and water uptakes of PVA/SSA and PVA/SSA/PEG membranes as a function of SSA content. The membranes are designated as T100 and T100C1 depending on the different cross-linking combination (where T100 indicates only thermal cross-linking at 100°C for an hour and C1 refers to chemical cross-linking for an hour). The SSA content and the degree of cross-linking in the membranes would play an important role in conductivity and water uptake. It can be seen that the conductivity reached the maximum of 0.0469 S cm^{-1} when PVA/SSA being 1:0.5 by mass and only thermal cross-linking at 100°C for an hour.

Figure 2 shows the thermogravimetric analysis curves of PVA/SSA membrane and PVA/SSA/PEG membrane with different cross-linking methods. All of the samples displayed three major weight loss stages at around 100-200, 230-350, and 370-520°C arising from the process of the thermal solvation, thermal desulfonation, and thermooxidation of the polymer matrix. As can be seen in the Figure 2, for the PVA/SSA-T100 and PVA/SSA/PEG-T100 membranes, the weight loss of the first stage was dropped from 10% to 5% after the addition of plasticizer PEG. It should be mentioned that the membranes with further chemical cross-linking seems to be more stable in the third weight loss stage, and the weight loss of PVA/SSA and PVA/SSA/PEG membranes dropped from 19.46% and 20.96% to 14.74% and 17.11%. This indicates that the cross-linking technique and the plasticizer PEG are both attributed to improve the thermal stability of the membranes.

References

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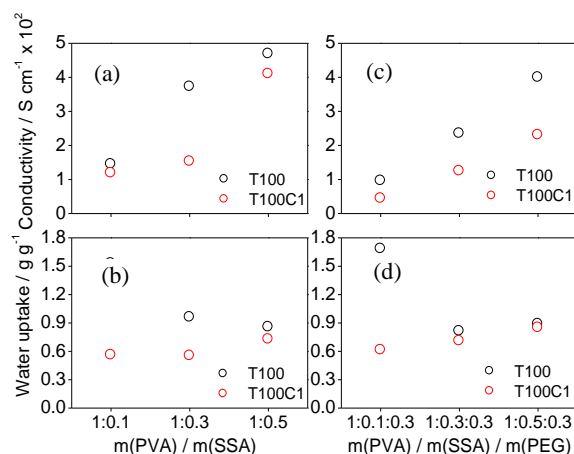


Figure 1. (a),(c) Proton conductivity and (b),(d) water uptake of PVA/SSA and PVA/SSA/PEG membranes as a function of SSA content in polymers with different cross-linking compositions.

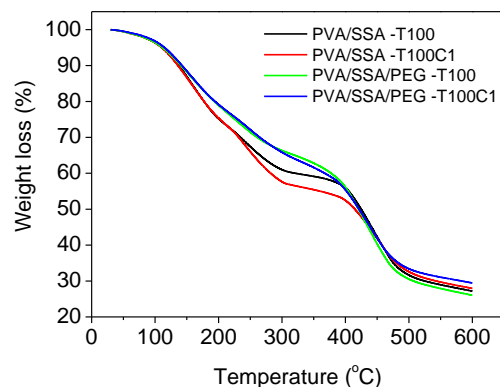


Figure 2. TGA thermograms of PVA/SSA and PVA/SSA/PEG membranes with different cross-linking compositions.