Synthesis and conductivity of multiwalled carbon nanotubes modified poly(vinyl alcohol)/ poly(diallyldimethylammonium chloride) as alkaline anion-exchange membranes

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The alkaline membrane fuel cells (AMFCs), which use the anion-exchange membranes to display the proton-exchange membranes with OH^- anions instead of H^+ ions, have evoked considerable attention due to their faster electrokinetics, lower fuel crossover, reduced CO poisoning, and use of non-precious metal catalysts [1]. In the development of AMFCs, alkaline anion-exchange membranes (AAEMs) play a critical role to make a breakthrough in AMFC performances. However, AAEMs are usually unstable in alkaline media especially at temperatures above 60°C and at high KOH concentrations. Recent research has focused on the introduction of multiwalled carbon nanotubes (MWCNTs) [2-3] or other inorganic filler [4] into matrix to improve the durability of the membranes. Compared to other inorganic fillers as conducting reinforcements, polymeric nanocomposites with MWCNTs can form a conducting path at relatively low concentrations owing to their high aspect ratios and high surface areas [5-7]. Based on this conception, we here report novel series of alkaline anion-exchange membranes, poly(vinyl alcohol)/ poly(diallyldimethylammonium chloride) (PVA/PDDA) modified MWCNTs with different structures.

The membranes were prepared by a simple solution-casting method, where PVA (99% hydrolyzed, average molecular weight Mw = 86,000-89,000; Aldrich) was fully dissolved in water to make a 10% solution at 90°C. PDDA (20% water solution, average Mw = 400,000-500,000, Aldrich). MWCNTs were then mixed with the above PVA solution to cast a membrane at ambient temperature. Three different MWCNTs were supplied by the AlphaNano Technology Co. Ltd., China, namely the pristine MWCNTs (purity > 95wt.%, length ~ 15□μm, diameter 30-50 nm,), carboxyl-functionalized MWCNTs (MWCNTs-COOH) (purity > 95wt.%, length ~ 10□μm, diameter 30-50 nm, -COOH 0.5-3wt.%) and hydroxyl-functionalized MWCNTs (MWCNTs-OH), (purity>95%, length ~ 10□μm, diameter 30-50 nm, -OH 1-7wt.%). Then the membranes were treated by thermal and chemical cross-linking procedures and ion-exchange with 2 M KOH solution. Standing and flat membranes were obtained with a thickness about 70-90 μm. The effects of thermal cross-linking temperature and MWCNTs addition on membrane proton conductivity are studied using AC impedance technique.

As a typical candidate, Fig. 1 shows the membrane pictures of PVA/PDDA and PVA/PDDA/MWCNTs, and Fig. 2 shows the ionic conductivity (σ_{Cl^-}) and water uptake (*WU*) of PVA/PDDA/MWCNTs membrane. In order to explore the most suitable thermal cross-linking temperature, the σ_{Cl^-} and *WU* of PVA/PDDA (1:0.5 by mass) membranes with the addition of 1 wt.% MWCNTs have been measured, while the thermal cross-linking time and chemical cross-linking time were both kept for 1 h. At this situation, the membranes were treated without KOH immersing and the conductivity is due to Cl^-, which is lower than the OH^- conductivity. From Fig. 2, we can see that the σ_{Cl^-} values increased greatly with increasing thermal cross-linking temperature and reached 8.73×10^{-3} S cm^{-1} when the heat-treatment temperature was at 160°C. For obtaining both good mechanical property and high conductivity of the membranes, in this work, the annealing temperature of 150°C for 1 h was found to be best condition for thermal cross-linking reaction. The details will be reported in the meeting.

References

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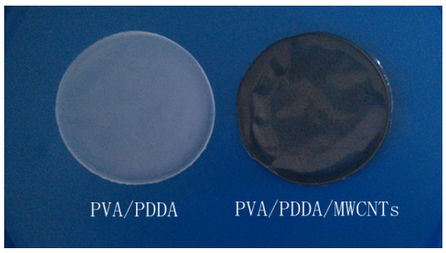

Fig. 1 Membrane pictures of PVA/PDDA membrane and PVA/PDDA/MWCNTs (1 wt.%) membrane. Polymer composition: PVA/PDDA = 1:0.5 by mass.

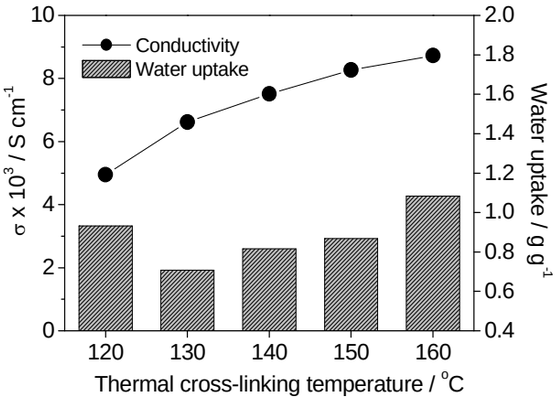

Fig. 2 Cl^- conductivity and *WU* of PVA/PDDA/MWCNTs (1 wt.%) as a function of thermal cross-linking temperature. Polymer composition PVA/PDDA = 1:0.5 by mass.