Mechanical properties and XRD of Nafion modified by 2-hydroxyethylammonium ionic liquids

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Abstract. In this work, the Nafion 112 membrane impregnated with 2-hydroxyethylammonium carboxylate ionic liquids have been investigated. The used ionic liquids were 2-hydroxyethylammonium formate [HEA]F, acetate [HEA]A and lactate [HEA]L. Prepared composite membranes Nafion/ionic liquid are characterized by mechanical testing, such as tensile test and creep test. It is found that ionic liquids decrease elastic modulus and creep compliance, but do not have significant effect on the tensile strength. Also, composite membranes were studied by wide angle X-ray diffraction. All ionic liquids shift the peak maximum to the lower angle. In this work, only biodegradable ionic liquids were used for composite preparation.

1. Introduction

Fuel cells are one of the promising alternative sources of clean energy. Proton exchange membrane fuel cell (PEMFC) is currently selected from many different types of fuel cells for energy back-up systems. A key component of this type of fuel cell is proton exchange membrane (PEM). Nafion membrane is the commonly used as PEM. High mechanical strength, excellent thermal and chemical stabilities are Nafion membrane advantages over others PEM. However, Nafion membrane has high cost and its proton conductivity is decreasing at high temperatures. Therefore, Nafion membrane needs to be modified. Nowadays, there are many ways how membrane can be modified, e.g. incorporating titanium oxide [1], zirconium phosphate [2], etc. Last trend is to use ionic liquids (ILs) due to their high conductivity, good thermal stability and wide electrochemical window [3,4]. There are two main methods how to modify membrane with an IL: solution casting method [5] and IL-swollen method [6]. The IL-swollen method was used in this work.

In this study, 2-hydroxyethylammonium carboxylates were used for the modification of Nafion membrane. These ILs are non-toxic and highly biodegradable [7,8]. The impact on conductivity and thermal stability with the same ILs has been studied in our previous research [9]. However, for practical applications the mechanical properties of composite membrane are very important. 2-hydroxyethylammonium lactate already was used for the modification of other type of PEM [10].
2. Experimental

2.1. Materials

Nafion 112 (equivalent weight 1100 g/mol, thickness 50.8 µm) was purchased from Ion Power. The ILs 2-hydroxyethylammonium formate [HEA]F, acetate [HEA]A, lactate [HEA]L (for chemical structures see figure 1) were synthesized in reaction of 2-hydroxyethylamine with formic, acetic or lactic acids by the method described elsewhere [7,8]. 2-Hydroxyethylamine and formic acid (90%) (Aldrich) were distilled before use. Others carboxylic acids were analytical grade commercial products (Aldrich). The ionic liquids purity is ≥98% for lactates and ≥99% for formates and acetates (by HPLC/MS).

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\begin{align*}
\text{[HEA]}F & \quad \text{[HEA]}A & \quad \text{[HEA]}L \\
\text{HO} & \quad \text{HO} & \quad \text{HO} \\
\text{NH}_3 & \quad \text{NH}_3 & \quad \text{NH}_3 \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{H} & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
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*Figure 1.* Chemical structures of used 2-hydroxyethylammonium carboxylate ionic liquids

2.2. Impregnation with ionic liquids

Nafion membrane samples were pretreated by sequential immersion in boiling 0.5 mol/L H_2SO_4 solution and then in boiling deionized water. After that membrane was blotted with a tissue to remove any residual liquid and thereafter dried at 80 °C in oven for 1 h. Impregnation with ionic liquids was performed by immersing the membrane samples into the corresponding IL at 50 °C temperature for 90 min. After impregnation the membranes surface was blotted with a tissue. Membranes were afterwards dried at 80 °C in oven until constant weight.

2.3. Characterizations

Stress-strain curves of the membrane samples were measured by a Tinius Olsen H1K-S UTM material testing machine. The membranes were cut into “dogbone” shaped specimens with the gauge length and width of 22 mm x 5 mm, respectively. Measurements were carried out at room temperature in air atmosphere with a constant deformation speed of 50 mm/min.

Creep test was performed at homemade apparatus at room temperature in air atmosphere. The membranes also were cut into “dogbone” shaped specimens with the same dimensions as in the previous experiment. Membranes specimens were clumped in the apparatus and a constant weight was hung from the bottom of the “dogbone” for 30 min. Elongation was recorded by a MarCator 1086 digital indicator.

Wide angle X-ray diffraction (XRD) patterns were recorded on Bruker D8 ADVANCE diffractometer. Diffraction spectra were measured using a Cu Kα source (λ_{Kα} = 1.54180 Å) operated at 40 kV and 40 mA. Scans were made from 5° to 60° 20. The scattering angle was increased by 0.02° 20 steps, with a time per step equal to 0.1 s.

3. Results and Discussion

3.1. Mechanical properties

The tensile stress at break of dry Nafion 112 membrane and its composites with ILs are shown on figure 2. It was found that the tensile strength is ~15 MPa for dry Nafion 112 membrane. Impregnated Nafion 112 membranes have the similar values as dry membrane. IL with acetate anion slightly increases tensile strength, but with lactate decreases it. The elastic moduli of dry and impregnated Nafion 112 membranes are shown on figure 3. The dry membrane has the highest elastic modulus (~250 MPa). The incorporation of ILs into the membrane decreases the elastic modulus value. The
biggest effect on the elastic modulus has [HEA]L. Composite with this IL has 2.5 times lesser elastic modulus (~84 MPa) than a pure membrane. Elastic modulus of composite with [HEA]F also is several times smaller than a pure membrane. At the same time [HEA]A does not significantly decrease elastic modulus of the Nafion 112 membrane.

Figure 2. Tensile stress at break of Nafion 112 and impregnated Nafion membranes.

Figure 3. Elastic modulus of Nafion 112 and impregnated Nafion membranes.

Figure 4 shows the short-time creep test. Since the membrane has the permanent pressure on its surface in PEMFC, it is important to know how the constant stress will affect on the membrane in time. Nafion 112/[HEA]L composite has the biggest creep compliance as compared with the others composites. The creep compliance of Nafion 112/[HEA]F is lower than composite with [HEA]L. The dry membrane and impregnated with [HEA]A have the similar creep compliances. The creep test results show the good matching with elastic modulus values from figure 3.

Figure 4. The short-time creep test data of dry Nafion 112 and impregnated Nafion membranes.

3.2. XRD measurements
The results of XRD measurements of dry Nafion 112 and its composite with ILs are shown on figure 5. The first maximum is attributed to the distance between two PTFE segments which form clusters in the membrane [2]. The dry Nafion 112 membrane has the peak with the maximum at ~18.1°. Composite membranes have the peak maximum at the similar 2θ, but these maximums are slightly shifted to the lower 2θ. This means that the distance increases between two PTFE segments.
Composites do not have the same shift value. The biggest shift have Nafion 112/[HEA]A and Nafion 112/[HEA]L – the peak maximum at ~17.8°, but Nafion 112/[HEA]F at ~17.9°.

Figure 5. The XRD data of Nafion/[HEA]F (a), Nafion/[HEA]A (b), Nafion/[HEA]L (c) and dry Nafion (d).

4. Conclusions
Composite membranes were prepared from Nafion 112 and three different biodegradable 2-hydroxyethylammonium ionic liquids: [HEA]F, [HEA]A and [HEA]L. After impregnation into membrane the used ionic liquids do not decrease the mechanical strength, but at the same time ionic liquids act as plasticizers and decrease the elastic modulus as well as increase the creep compliance. Also, all ionic liquids increase the distance between two PTFE segments according to XRD spectra. The Nafion/[HEA]A has potential to be used in PEMFC according to its good mechanical properties. The PEMFC working temperature is about 80 °C, so the mechanical properties at higher temperatures need more investigation, because mechanical properties depend on glass transition temperature.

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