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Synthesis of PVA/imidazole/SiO_2 hybrid membrane

Imidazole ($C_3H_4N_2$, Wako, Japan), tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS, 99.9 %, Colcote, Japan) and poly(vinyl alcohol) with a molecular weight of 100,000 g/mol (Nacalai Tesque, Japan) were used as raw materials. De-ionized water was purified using a Millipore Gradient Milli-Q® water purification system. Solvents and reagents of analytical grade were commercial products and used as obtained.

The hybrid membranes were prepared by a sol-gel process. An appropriate amount of PVA was dissolved in deionized water and stirred at 90 °C. Imidazole was also dissolved in deionized water, stirred at 80 °C for 4 h after which the two mixtures were mixed together and stirred at 90 °C for 12 h, to obtain an aqueous solution. The solution was then cooled to room temperature and 2 ml of TEOS was added. Gelation process was carried out for 12 h. The final solution was cast on a glass plate or Teflon mold to a desired thickness and dried at room temperature for 1 week. This was followed by a heat treatment at 60 °C for 6 h under nitrogen condition. The preparation flow chart and structure of the hybrid network are shown in Fig. S1.

Surface morphology

Fig. S2 illustrates surface morphology of the PVA/imidazole/SiO_2 hybrid membranes by SEM micrographs with various magnifications. The surface morphologies of the materials were observed at several angles (10–50 μm). The micrographs in Fig. S2 a-e, display a dense structure, because of well dispersion of SiO_2 and imidazole in the composite film. The concentrations of PVA and imidazole

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were significant factors affecting the formation of these homogenous gels by sol-gel method. Completely mixed phases were observed on the surface of the formed composite membrane without separation. Fig. S2a-e reveals that smooth and ionic clusters were formed on the surface of the composite membrane. These ionic clusters facilitate the transportation process of proton; therefore, the corresponding proton conductivity would be enhanced.

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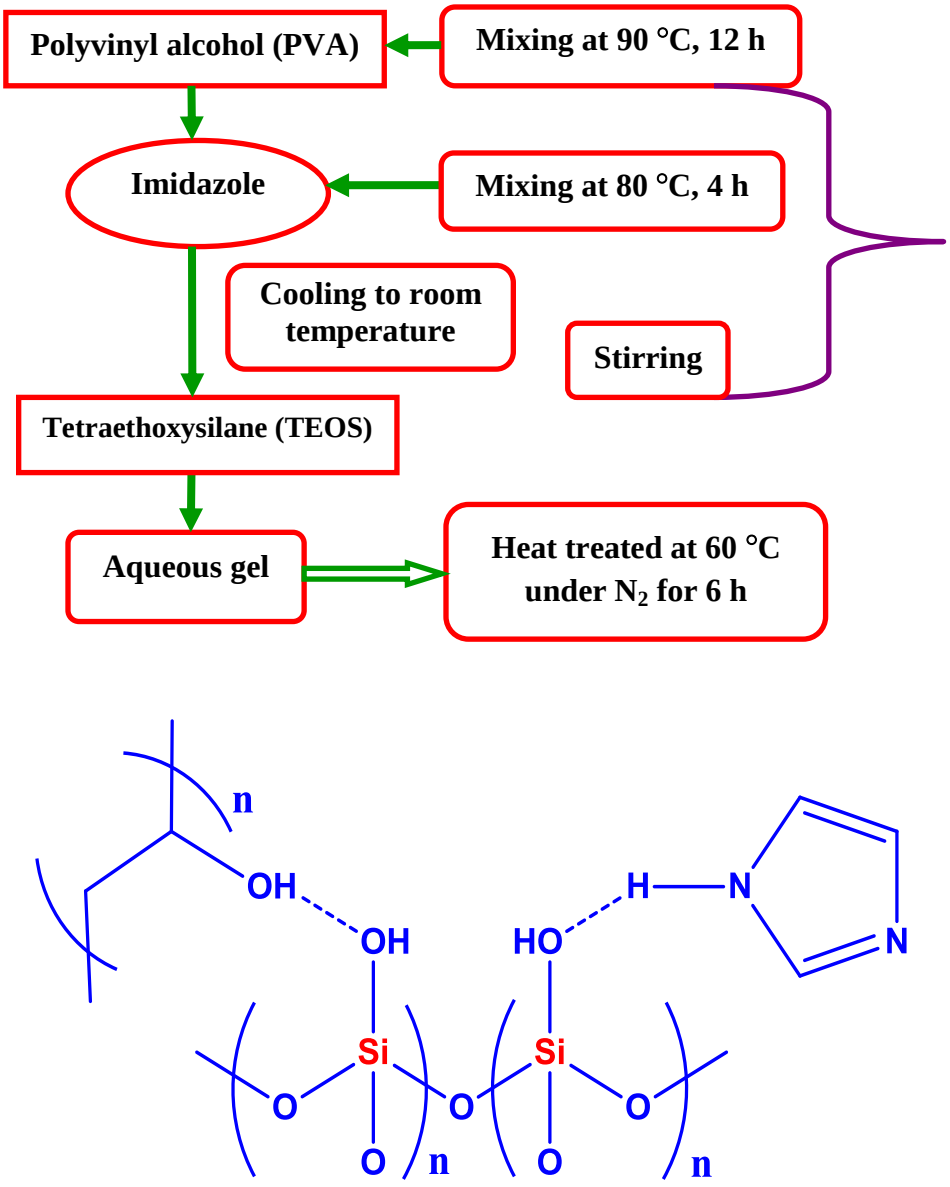

Fig. S1 A flow chart of the preparation and the structural networks of the PVA/imidazole/SiO_2 hybrid membrane.

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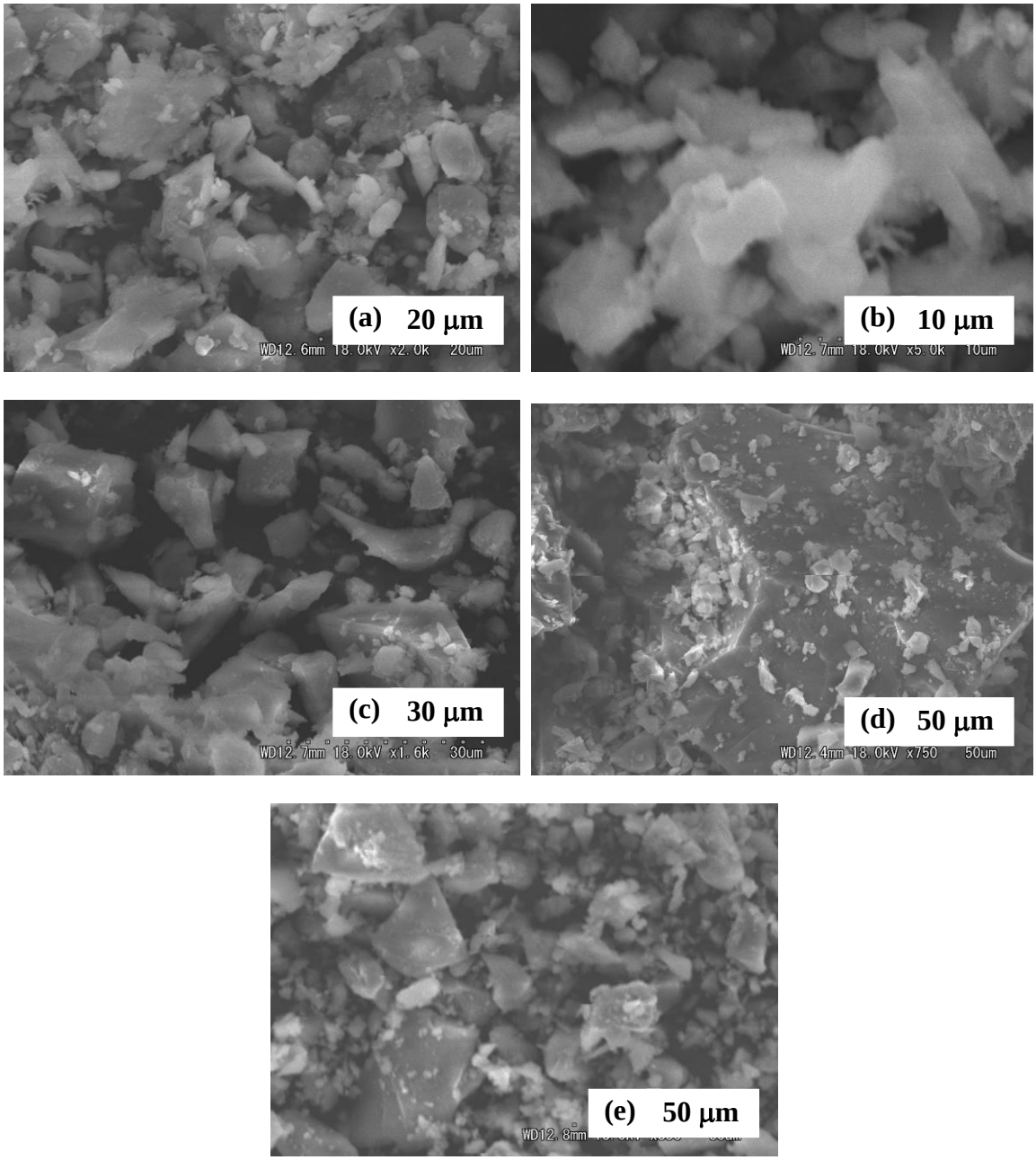

Fig. S2 SEM micrographs of the PVA/imidazole/SiO_2 hybrid composite membranes: (a) 90/10 wt%/2 ml, (b) 80/20 wt%/2 ml, (c) 70/30 wt%/2 ml, (d) 60/40 wt%/2 ml and (e) 50/50 wt%/2 ml.