

# The zwitterion effect in proton exchange membranes as synthesised by polymerisation of bicontinuous microemulsions

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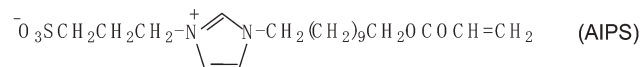
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The bicontinuous microemulsions consisting of a polymerisable zwitterionic surfactant 3-((11-acryloyloxyundecyl)imidazolyl) propyl sulfonate (AIPS) and other monomers can be cross-polymerised to form good proton conductive membranes.

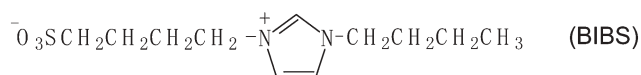
Proton conducting polymers are of great importance due to their possible application in proton exchange membrane (PEM) fuel cells. The membrane acts as a separator to prevent the mixing of reactant gases and as an electrolyte for transporting proton from anode to cathode. Nafion<sup>®</sup> is currently the most commonly used perfluorosulfonic acid (PFSA) membrane in fuel cells for its good proton conductivity ( $0.1 \text{ S cm}^{-1}$ ) and stability.<sup>1</sup> But it is expensive and not environmental friendly.<sup>2</sup> The challenge is to develop cheaper non-fluorinated or only partially perfluorinated PEMs for some fuel cell applications.<sup>1,3-8</sup> Here we demonstrate a novel method for synthesizing nanostructured PEMs of high proton conductivity ( $0.1\text{--}0.15 \text{ S cm}^{-1}$ ) by direct polymerisation of bicontinuous microemulsions containing a zwitterionic surfactant and fluorine-free components. Some of these PEM membranes have been tested in a single fuel cell, which exhibited good current–voltage polarization curves. The use of the polymerisable zwitterionic surfactant AIPS as a nanostructural template in water is the key factor for the successful synthesis of new PEMs with relatively high conductivity.

We have previously demonstrated that transparent nanostructured membranes<sup>9</sup> could be synthesised by the polymerisation of bicontinuous microemulsions containing a polymerisable zwitterionic surfactant, AUDMMA ( $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ ), MMA and water. In the present study, we synthesized a new zwitterionic surfactant (AIPS)<sup>†</sup> that consists of an imidazolylpropyl sulfonate polar head group and a polymerisable hydrophobic tail as



The critical micelle concentration (CMC) of AIPS surfactant is  $1.35 \times 10^{-3} \text{ M}$  at  $30^\circ\text{C}$ .

A similar hydrophilic segment of 1-butylimidazolium-3-(n-butanesulfonate) [BIBS] is cited here<sup>10</sup> for the structural comparison.



Unlike the polymerisable surfactant AIPS, BIBS is neither a surfactant due to the shorter hydrophobic chains nor a polymerisable monomer because it has no vinyl group. But BIBS has been shown to exert a positive zwitterion effect<sup>10</sup> on the dissociation of lithium ion-polyelectrolytes. We illustrate here that a similar zwitterion effect is also being observed for our PEMs consisting of polymerized AIPS.

Three components consisting of polymerisable surfactant AIPS (35 wt%), methylmethacrylate (MMA) (35 wt%) and water (30 wt%) were sufficient to form a basic bicontinuous microemulsion. The formulation also contained 0.2 wt% of 2,2-dimethoxy-2-phenylacetophenone (DMPA), an UV initiator for free radical polymerization. This transparent liquid microemulsion was sandwiched by two glass plates and it was polymerised in an UV reactor (Hg lamps) for about 2 h to form a transparent PEM membrane (PEM 1) of about  $120 \mu\text{m}$  thickness. But this basic membrane had a low conductivity of only  $0.007 \text{ S cm}^{-1}$  as measured at  $25^\circ\text{C}$ . Hence the sulfonic monomer SPM ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{SO}_3\text{K}$ ) was chosen to incorporate into the formulation as shown in Table 1. After adding 12.5, 11.5 and 10.0 wt% SPM to the basic formulation (PEM 2, 3, 4) with the increasing water content from 25.0, 30.0 to 40.0 wt%, the proton conductivity increased sharply from  $0.007 \text{ S cm}^{-1}$  to 0.10, 0.12 and  $0.15 \text{ S cm}^{-1}$ , respectively. The addition of SPM was to provide additional conducting sulfonic ions and hence protons after the PEMs were treated by dilute  $\text{H}_2\text{SO}_4$  followed by washing them thoroughly with deionized water. The mechanical strengths of these PEMs were improved by incorporating 1.0 wt% of ethylene glycol dimethacrylate (EGDMA) as a cross-linker in the

**Table 1** Bicontinuous microemulsion compositions for synthesizing some basic PEMs

	PEM compositions (wt%)			
	1	2	3	4
AIPS	34.0	29.0	29.0	29.0
SPM	—	12.5	11.5	10.0
MMA	35.0	32.5	28.5	20.0
Water	30.0	25.0	30.0	40.0
EGMDA	1	1	1	1
	PEM membrane			
Conductivity/ $\text{S cm}^{-1}$ at $25^\circ\text{C}$	0.007	0.10	0.12	0.15
Storage modulus/MPa	22.30	11.74	12.99	8.057
EW/g $\text{mol}^{-1}$	985	1140	1070	990

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formulation. The storage modulus of the PEMs after acid treatment ranged from about 8 to 22 MPa. The equivalent weight (EW) for PEMs 2–4 varied slightly from 990 to 1140 g mol<sup>-1</sup>. The acid treated PEMs 2–4 would take up additional 10–15 wt% water.

The SEM images in Fig. 1 clearly show the nanostructures of the polymer domains (white winding strips) and the aqueous channels (black winding strips) for PEMs 1–4 respectively. The aqueous channels ranging from 20 to 50 nm in width were randomly distributed as a sponge structure that provides an unrestricted surrounding for the movement of water molecules. The similar bicontinuous nanostructures of a bicontinuous microemulsion have been simulated by Pieruschka and Marcelja.<sup>11</sup>

A schematic presentation (Fig. 2) of the bicontinuous nanostructures of polymer and aqueous domains with the polar groups of AIPS and SPM at the interfaces may be used to explain our results. As both AIPS and SPM molecules consist of both hydrophobic and hydrophilic segments, they would preferably situate along the interfaces between aqueous and hydrocarbon domains of the bicontinuous microemulsion prior

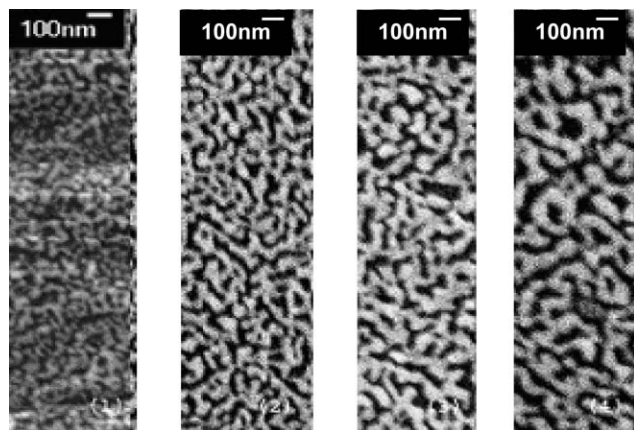


Fig. 1 SEM images for PEMs 1–4, where white and black winding strips represent polymer domains and aqueous channels respectively.

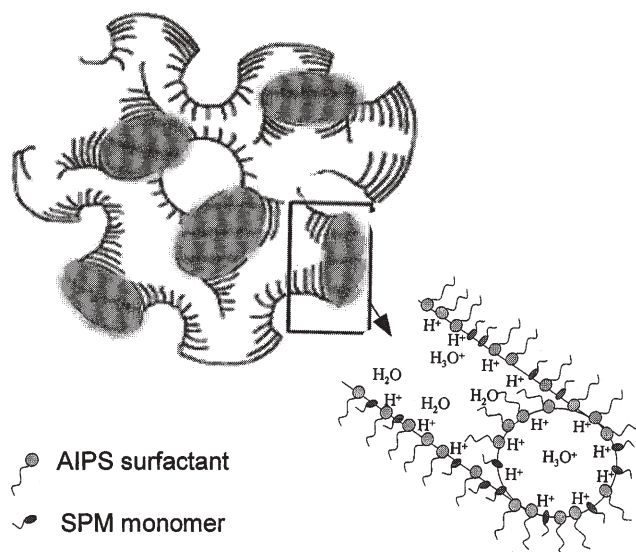


Fig. 2 A schematic presentation of bicontinuous nanostructures of the as-synthesized PEM.

to polymerisation. Once the vinyl groups of AIPS, SPM and EGDMA were cross-polymerised with MMA, the polymer domains were tightly cross-linked to provide the mechanical strength of PEM. As a result, the hydrophilic portions of AIPS and SPM would protrude into the aqueous domains forming numerous aqueous channels as revealed in Fig. 2. The immobilized sulfonate salt derived from SPM was converted to sulfonic acid by treating the prepared membrane with dilute H<sub>2</sub>SO<sub>4</sub>. The dissociation of sulfonic acid could be enhanced by the zwitterion effect through their ionic interactions at the close proximity to the zwitterions of the immobilized AIPS in PEMs 2–4. In other words, the sulfonic acid as derived from addition of SPM might preferentially interact with the sulfonate group on the zwitterions of AIPS to facilitate the dissociation of the sulfonic acid.

When only AIPS was replaced by a nonionic polymerisable surfactant (CH<sub>2</sub>=CHCOO(CH<sub>2</sub>)<sub>11</sub>–(OCH<sub>2</sub>CH<sub>2</sub>)<sub>40</sub>OCH<sub>3</sub>)<sup>12</sup> in the formulation, the proton conductivity of PEMs 2–4 was sharply reduced by an order of magnitude to about 0.013 S cm<sup>-1</sup>. This indirectly substantiates the zwitterion effect exerted by AIPS in promoting proton conductivity for PEMs.<sup>2–4</sup>

The conductivity of PEM arises from the proton migration not only near the vicinity of aqueous interfaces *via* the known Grotthus proton hopping mechanism,<sup>13</sup> but also *via* the diffusion through the medium together with water molecules in the PEM resulting in higher overall proton conductivity. Our previous study<sup>14</sup> has shown that the water molecules did not experience barriers in the polymerised bicontinuous microemulsion using AUDMAA zwitterionic surfactant.<sup>9</sup>

The performance of a single fuel cell is described by its polarization curve, *i.e.*, cell voltage *vs.* current density as shown in Fig. 3. The performance of PEM 1 with no SPM was extremely poor as can be seen from the inset in Fig. 3. The other three membranes containing 10–12.5 wt% SPM exhibited good *I–V* curves, with a maximum power density of about 0.5 W cm<sup>-2</sup>. Further improvement of these membranes for fuel cell applications is currently under study.

This novel microemulsion polymerisation technique also enables one to freely modify microemulsion formulations for transforming them into nanostructured materials of various functionalities.

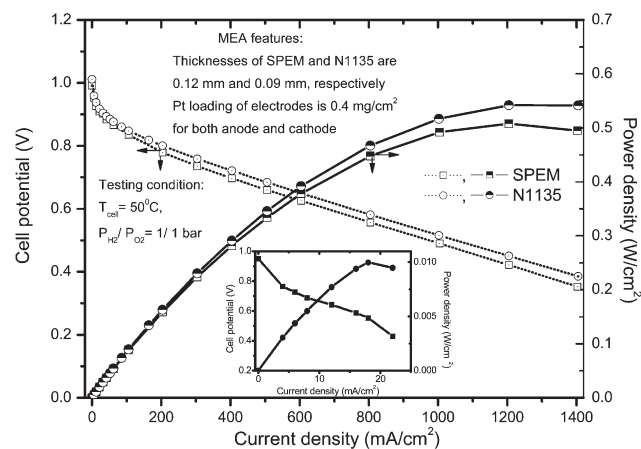
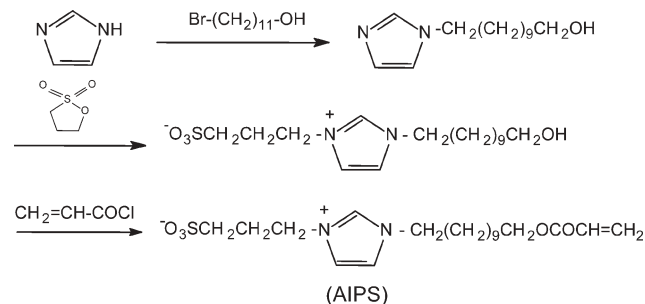


Fig. 3 Single cell performance using membrane PEM 3 containing 11.5 wt% SPM and the inset for PEM 1 without SPM. N1135 represents Nafion 1135 membrane.

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## Notes and references

† The polymerisable zwitterionic surfactant, 3-((11-acryloyloxyundecyl)imidazolyl) propyl sulfonate (AIPS), was synthesized as below.



In brief, the first step involved the synthesis of 11-hydroxyundecylimidazole by reacting 11-bromoundecanol with imidazole by a  $S_N2$  reaction mechanism and then subject to sulfonation of precursor intermediate using 1,3 propane-sultone to the corresponding sulfonate (3-((11-hydroxyundecyl)imidazolyl) propyl sulfonate). The final introduction of an acrylate group to the precursor sulfonate produced the desired zwitterionic surfactant AIPS with a polymerisable tail group. The precursor intermediates and the surfactant monomer were obtained in good yields of reasonable purity, as indicated by  $^1\text{H}$  NMR spectra.

The measurement of proton conductivity at room temperature under fully hydrated conditions was performed by connecting the EG&G model 273 to a EG&G model 5210 lock-in amplifier over a frequency range of 1 mHz to 100 kHz.

The storage moduli of the acid-treated membranes were measured in triplicates by a Dynamic Mechanical Analyzer (TA Instruments, DMA 2980). The EW (equivalent weight) was determined by titrating the acid form of the membrane with NaOH solution (0.025 M) to the phenolphthalein end-point. EW was calculated from the dried weight of the membrane in grams divided by moles of NaOH used.

For the polarization measurements, a single cell was operated at 50 °C and 1 bar for both  $\text{H}_2$  and  $\text{O}_2$  without humidification using Arbin Electronic load and PC with MITS software. The anode and cathode sheet were a carbon paper (SGL, Germany) with carbon-supported 20 wt% Pt catalyst layer supplied by E-TEK, Natick, MA. The catalyst loadings at the anode and cathode were  $2 \text{ mg cm}^{-2}$ , thus, Pt loadings at the anode and cathode were  $0.4 \text{ mg cm}^{-2}$ . The effective electrode area was  $5 \text{ cm}^2$ . The gas flow rate was kept at a fixed stoichiometry (1.15 times stoichiometric for  $\text{H}_2$  and 2 times stoichiometric for  $\text{O}_2$ ) at  $1 \text{ A cm}^{-2}$  current density.

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