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Imidazolium methanesulfonate as a high temperature proton conductor

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1. Schematic of the three-electrode system

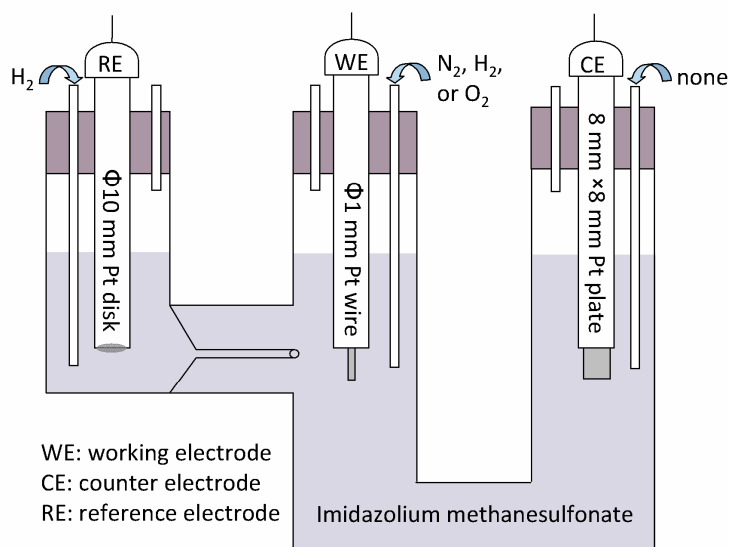
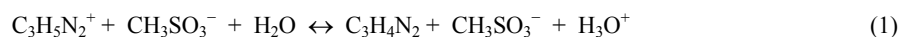


Fig. S1 Schematic of the three-electrode system.

2. Calculation of ionization in aqueous solution

Since the salt dissolves in water and becomes hydrated after ionization, an ultra diluted solution of the salt is formed given that the mass fraction of the salt is 0.100 %, according to the equations below:



At room temperature:

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

Assume 1.00 kg solution of the salt, then $m(\text{salt}) = 0.100 \% \times 1.00 \text{ kg} = 1.00 \text{ g}$.

While

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 4.80$$

$$[\text{H}_3\text{O}^+] \gg [\text{OH}^-]$$

Therefore, the contribution to $[\text{H}_3\text{O}^+]$ from (2) can be neglected, indicating:

$$[\text{H}_3\text{O}^+] + [\text{C}_3\text{H}_5\text{N}_2^+] = [\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-]$$

Hence

$$[\text{C}_3\text{H}_5\text{N}_2^+] = [\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-] - [\text{H}_3\text{O}^+] = [\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-] - 10^{-\text{pH}}$$

Meanwhile

$$[\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-] = \frac{n(\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-)}{V}$$

$$n(\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-) = \frac{m(\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-)}{M(\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-)} = \frac{1.00 \text{ g}}{164.18 \text{ g mol}^{-1}} = 0.00609 \text{ mol}$$

$$V \approx \frac{m_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{999 \text{ g}}{997 \text{ g L}^{-1}} = 1.00 \text{ L}$$

Therefore

$$[\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-] = 0.00609 \text{ mol L}^{-1}$$

$$[\text{C}_3\text{H}_5\text{N}_2^+] = [\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-] - 10^{-\text{pH}} = (0.00609 - 10^{-4.80}) \text{ mol L}^{-1} = 0.00608 \text{ mol L}^{-1}$$

Eventually, the ionicity of the salt in the aqueous solution can be estimated as:

$$\frac{n(\text{C}_3\text{H}_5\text{N}_2^+)}{n(\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-)} = \frac{0.00608}{0.00609} = 99.8\%$$

The presence of CH_3SO_3^- anion in the aqueous solution has also been confirmed previously by ion chromatography quantitatively.⁴⁰ The high ionization of $\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{CH}_3\text{SO}_3^-$ ($\Delta\text{p}K_a \approx 9$) in its aqueous solution is consistent with the work of MacFarlane *et al.*^{S1} that the desired 99% ionization of PILs in aqueous solution can be achieved, in principle, at $\Delta\text{p}K_a = 4$. (Herein, $\Delta\text{p}K_a = \text{aqueous p}K_a \text{ value of the base} - \text{aqueous p}K_a \text{ value of the acid}$.)

3. DSC trace of a larger temperature range recorded at 10 K min⁻¹

Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 204 F1 Phoenix® under a N₂ atmosphere. Samples with approximately 10 mg each were tightly sealed in Al pans. The samples were heated to +230 °C and then cooled to -150 °C and heated again to +230 °C at cooling and heating rates of 10 K min⁻¹. DSC thermograms were recorded during the reheating scans.

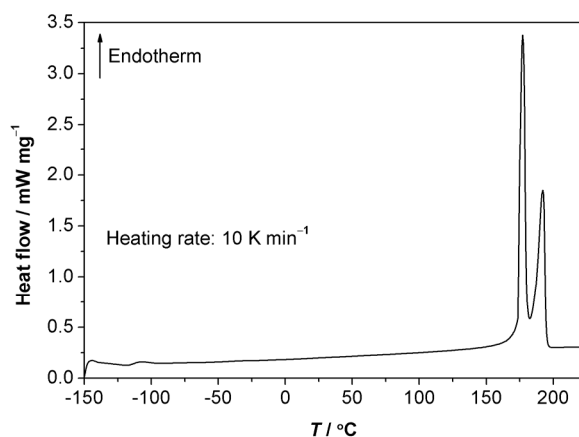


Fig. S2 DSC trace of 1 with a larger temperature range recorded at 10 K min⁻¹.

4. Enlarged view of temperature-dependent powder XRD patterns

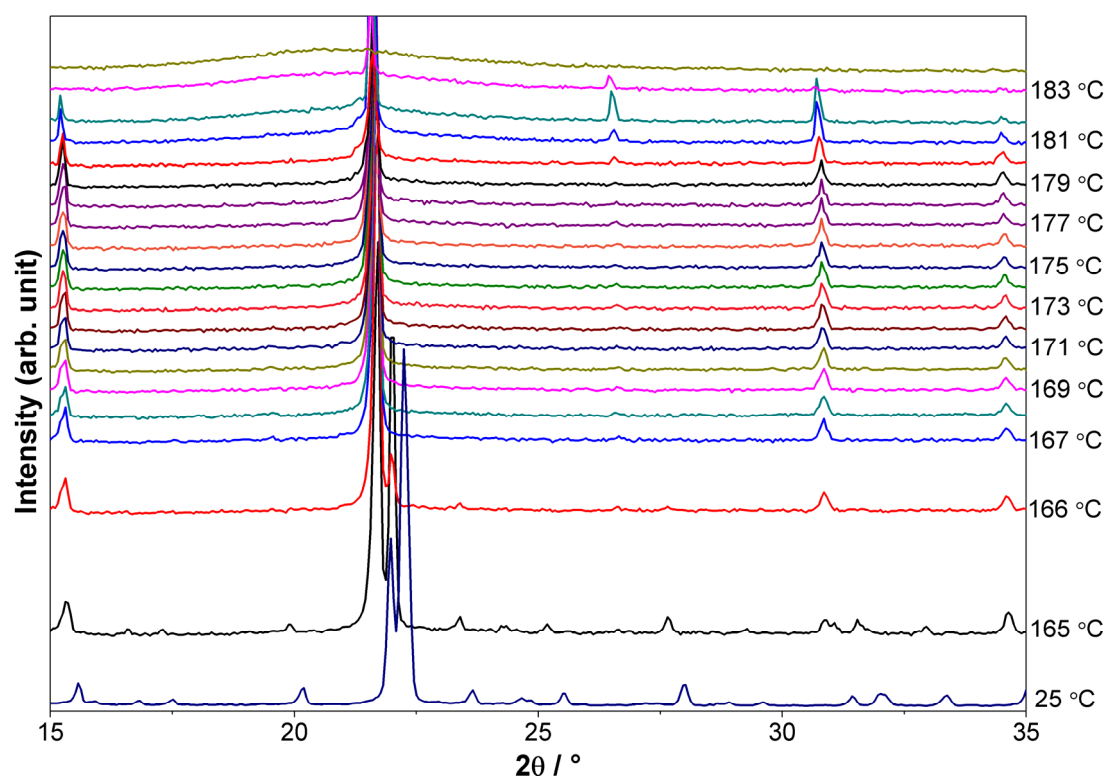


Fig. S3 Enlarged view of temperature-dependent powder XRD patterns of 1.

5. GIXRD patterns of the composite Nafion membrane at different incident angles

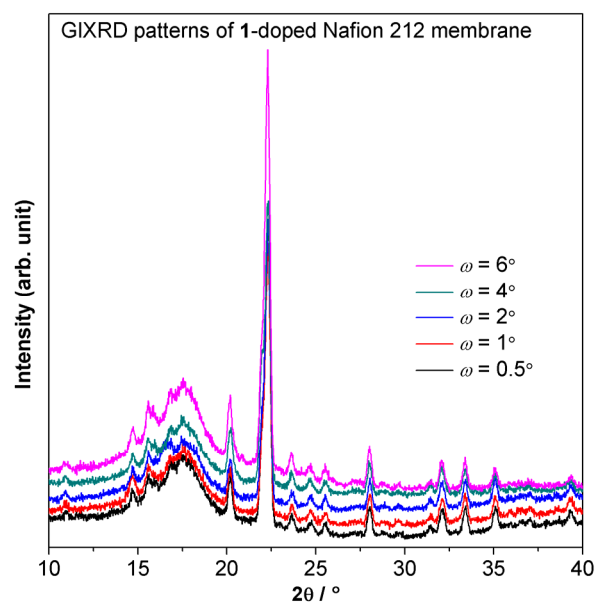


Fig. S4 GIXRD patterns of the composite Nafion membrane at different incident angles.

References:

- 40 J. Luo, T. V. Tan, O. Conrad and I. F. J. Vankelecom, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11441.
S1 D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth and M. Forsyth, *Chem. Commun.*, 2006, 1905.