Highly Conductive Anion-Exchange Membranes from Microporous Tröger's Base Polymers

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Abstract: *The development of polymeric anion-exchange membranes (AEMs) combining high ion conductivity and long-term stability is a major challenge for materials chemistry. AEMs with regularly distributed fixed cationic groups, based on the formation of microporous polymers containing the V-shape rigid Tröger's base units, are reported for the first time. Despite their simple preparation, which involves only two synthetic steps using commercially available precursors, the polymers provide AEMs with exceptional hydroxide conductivity at relatively low ion-exchange capacity, as well as a high swelling resistance and chemical stability. An unprecedented hydroxide conductivity of 164.4 mS cm^{-1} is obtained at a relatively a low ion-exchange capacity of 0.82 mmol g^{-1} under optimal operating conditions. The exceptional anion conductivity appears related to the intrinsic microporosity of the charged polymer matrix, which facilitates rapid anion transport.*

Anion-exchange membranes (AEMs) contain fixed positively charged groups within the polymer matrix, which allows the selective transport of hydrated anions such as OH^-, Cl^-, and HCO_3^- across the membrane.[1] They are an important component in many electrochemical and diffusion processes that require selective anion transport and high conduction combined with chemical stability. Their use is ubiquitous in industrial processes such as electrodialysis, diffusion dialysis, removal or recovery of metal ions from process streams,[2] and electrolysis.[3] More recently, in the energy storage and generation field, there has been renewed interest in developing chemically stable and highly conductive AEMs for redox flow batteries[4] and for anion-exchange membrane fuel cells

(AEMFC),[5] the latter being of interest primarily because the high pH operating conditions allow cost reductions through the use of non-precious metal catalysts. Advantages also include the faster electrode reaction kinetics and flexible fuel choices.[6] However, the development of suitable AEMs for fuel cells remains a particularly demanding challenge for materials science, as the AEMs must combine high anionic conductivity with mechanical stability towards swelling in aqueous media and long-term chemical stability at high pH values. To date, many polymers have been investigated, mostly based on quaternized amines, with the aim of providing a high concentration of cationic sites. However, only a few have demonstrated sufficient stability together with high ionic conductivity for practical application.[7]

Recently, polymers prepared from diamine monomers using the highly efficient formation of Tröger's base (TB), a V-shaped bridged bicyclic aromatic diamine, demonstrate exceptional potential for gas separation membranes due to the high rigidity and intrinsic microporosity imparted by the TB unit.[8] The inefficient packing of the contorted polymer chains provides an intrinsic microporosity that facilitates rapid transport of gases, and their extreme rigidity provides selectivity for one gas over another. Additionally, the efficient transport of ions has been demonstrated within these TB polymers, allowing the fabrication of ionic diodes[9] and protective membranes for electrodes.[10] Herein, we report for the first time AEMs derived from quaternized TB polymers. Their intrinsic microporosity is anticipated to enable the rapid and efficient transport of anions. Despite the great diversity of cationic groups that have been incorporated into polymers with the objective of producing stable and high-performance AEMs, as far as we are aware, TB-containing polymers have not been investigated for this application.

The three polymers selected for this study can be defined by the structural components that are fused together by the TB unit to form the polymer chain: dimethyldiphenylmethane (DMDPM-TB), dimethylbiphenyl (DMBP-TB), and triptycene (Trip-TB). The synthesis of both DMDPM-TB[11] and Trip-TB[8b] was reported previously, with the latter being particularly promising for gas separations. DMBP-TB was prepared specifically for this study to provide a new TB-polymer of intermediate overall rigidity between the relatively flexible DMDPM-TB and the highly rigid Trip-TB (Scheme 1). DMBP-TB is synthesised by the reaction of commercially available 4,4′-diamino-3,3′-dimethylbiphenyl with dimethoxymethane using trifluoroacetic acid as the solvent (see the Supporting Information for details). As expected, the intrinsic microporosity of the three TB polymers increases with the overall chain rigidity as demonstrated

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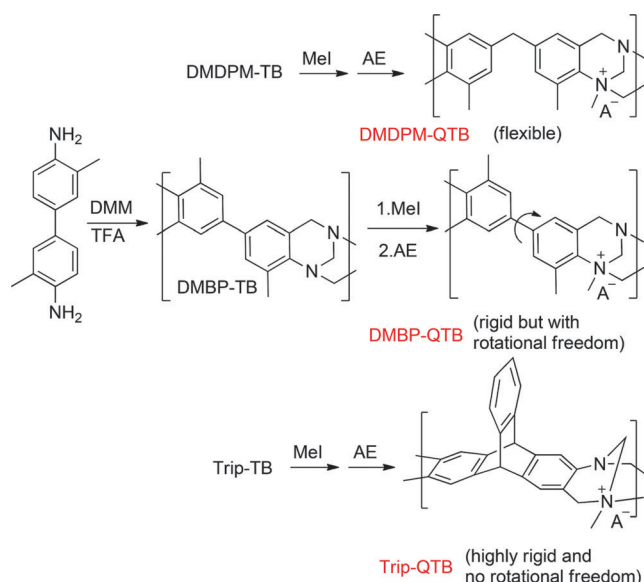
Scheme 1. The synthesis of the TB-polymer-based AEM materials. The non-quaternized polymers DMDPM-TB and Trip-TB were prepared as described previously.[8b, 11] AE = anion exchange, DMM = dimethoxymethane, TFA = trifluoroacetic acid, A⁻ = Cl⁻, HCO₃⁻, or OH⁻. The quaternized polymers (or membranes) were designated as DMDPM-QTB, DMBP-QTB and Trip-QTB, respectively.

by their apparent Brunauer–Emmett–Teller (BET) surface areas, which were calculated from nitrogen adsorption isotherms collected at 77 K (Table 1).

Robust and transparent films of each TB polymer, cast from chloroform solutions, were reacted with methyl iodide (MeI) to provide polycationic materials through quaternization, and the resulting quaternized films are designated as QTB. By analogy with the results from a previous study on the methylation of TB, this process is assumed to occur on only one of the two available tertiary amines through an S_N2 mechanism.[12] If desired, simply adjusting the amount of MeI used or the reaction time readily controls the degree of quaternization. Using an excess of MeI provides each polymer with a high degree of quaternization as confirmed by both ^{1}H NMR spectroscopy and AgNO₃ titration. The ion-exchange capacity (IEC) of these films was calculated using

Table 1: The properties of the TB polymers and the quaternized (QTB) membranes.

Polymer (AEM)	DMDPM-TB	DMBP-TB	Trip-TB
M_w [g mol⁻¹][a] (TB)	95 000	49 000	51 000
SA_{BET} [m² g⁻¹][b] (TB)	38	339	899
IEC [mmol g⁻¹][c] (QTB)	0.81	0.82	0.91
WU [%, 30 °C][d] (QTB)	8.6	36	81
P_{MeOH} [cm² s⁻¹][d] (QTB)	3.9×10^{-8}	9.1×10^{-8}	1.7×10^{-6}

[a] Of non-quaternized polymer measured by gel-permeation chromatography (GPC) against polystyrene standards. [b] N₂ adsorption isotherms at 77 K of the powdered form of the non-quaternized polymers (note that quaternized polymers do not adsorb significant quantities of N₂). [c] Of quaternized polymers measured by ^{1}H NMR and AgNO₃ titration of Cl⁻-exchanged polymer. [d] Of OH⁻-exchanged polymers. M_w = molecular weight, SA_{BET} = BET surface area, IEC = ion exchange capacity, WU = water uptake, P_{MeOH} = permeability of methanol.

Mohr's method and found to be in the range of 0.81–0.91 mmol g⁻¹, which is a relatively low value compared with many reported AEMs (Table 1). Subsequent exchange of the I⁻ for OH⁻ (or HCO₃⁻ or Cl⁻) could be achieved by simply treating the films with an aqueous solution of NH₄OH (or a suitable salt).

The mechanical robustness of its hydrated state is of crucial importance to the performance of a potential AEM, and this property can be degraded due to the absorption of excessive amounts water. Hence, water uptake (WU) measurements on the OH⁻ anion-exchanged films were performed, showing uptake values following the series DMDPM-QTB < DMBP-QTB < Trip-QTB (Table 1), with the value for DMDPM-QTB being remarkably low (WU = 8.6 wt %). This prompted a detailed study of the WU values and swelling of a film of DMDPM-QTB at temperatures up to 80 °C, showing that its excellent structural resilience to water uptake is maintained even over the likely working temperature range of an AEMFC (Supporting Information, Table S1). In contrast, Trip-QTB adsorbs more water, which is consistent with its higher intrinsic microporosity. The chemical stability of an AEM is also very important and was evaluated by immersion of the OH⁻ exchanged films in 2 M NaOH aqueous solutions maintained at 60 °C for 240 h. For DMDPM-QTB and DMBP-QTB no degradation was detected by ^{1}H NMR (Supporting Information, Figure S8), which is unexpected given the well-established tendency for quaternary ammonium cations to degrade under such harsh conditions. However, for Trip-QTB (OH⁻), degradation was apparent (Supporting Information, Table S2). This difference in chemical stability may also be related to the far greater water uptake within this polymer.[13] Finally, it is desirable that methanol, a potential fuel for AEMFCs, should have relatively low permeability through the AEM. This was confirmed for the OH⁻ exchanged films for DMDPM-QTB and DMBP-QTB but was significantly higher for Trip-QTB as expected from its greater intrinsic microporosity (Supporting Information, Figure S12).

Owing to their excellent structural and chemical stability, as well as their low methanol permeability, quaternized films of both DMDPM-TB and DMBP-TB were investigated further for their potential as AEMs by measuring their anionic conductivity (Cl⁻, HCO₃⁻, and OH⁻)[14] using the four-point probe technique over the temperature range 30–80 °C (Figure 1). Due to its inferior stability towards aqueous NaOH, only the conductivity of Cl⁻ was measured for Trip-QTB. As expected from its greater mobility in pure water (Supporting Information, Table S3), the OH⁻ anion shows the highest conductivity (σ_{OH^-}), with values ranging for DMDPM-QTB from 43.4 mS cm⁻¹ at 30 °C to 97.2 mS cm⁻¹ at 80 °C and for DMBP-QTB from 23.5 mS cm⁻¹ at 30 °C, rising sharply to 164.4 mS cm⁻¹ at 80 °C. DMBP-QTB demonstrates the highest value for σ_{OH^-} at 80 °C reported to date (Supporting Information, Table S4). Indeed, these values of σ_{OH^-} for both DMDPM-QTB and DMBP-QTB are exceptional considering the relatively low values of IEC for these polymers. It can be concluded that the TB units provide a close and regular distribution of cation groups, which allows their coordination hydration shells to overlap sufficiently well
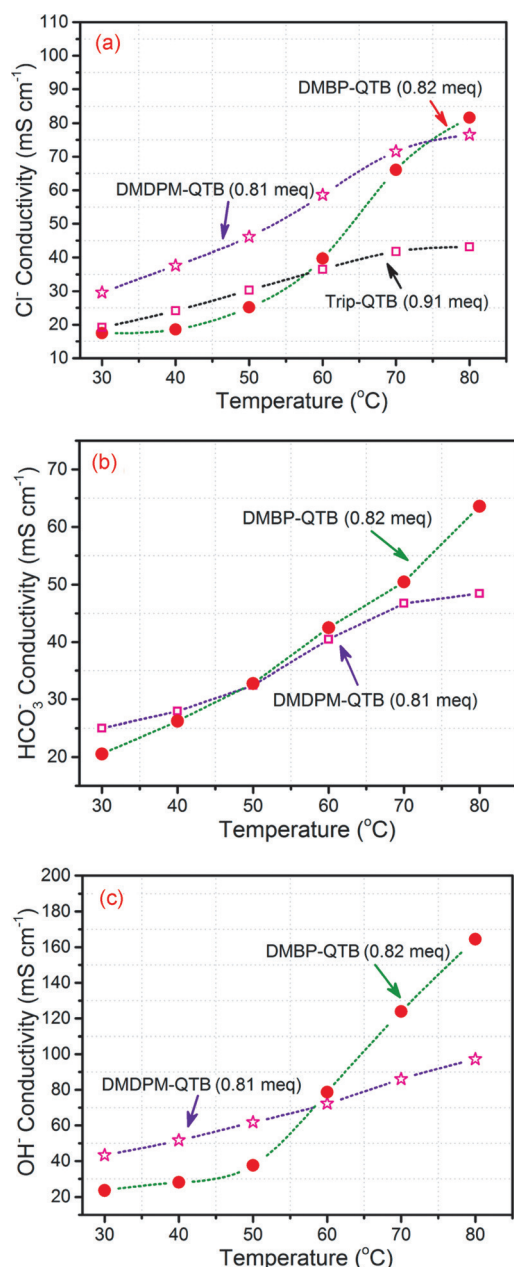
Figure 1. The conductivity of a) Cl^-, b) HCO_3^-, and c) OH^- in the quaternized TB polymers over the temperature range 30–80°C.

to facilitate efficient transport.[6a] The difference in conductivity regimes over the measured temperature range can be attributed to differences in the transport mechanism. The Cl^- and HCO_3^- ions are mainly transported through a vehicular mechanism, while OH^- ions are transported by both vehicular and Grotthuss mechanisms, the latter being a thermally activated hopping, which is the preferred mode at higher temperatures.[15]

Comparing the effect of the temperature on σ_{OH^-} of the two AEMs over the range 30–80°C, it is clear that there is a much greater temperature dependence for DMBP-QTB compared with DMDPM-QTB, for which the weaker dependence is similar to that of previously reported polymers (Figure 1).[13,16] This difference is likely related to the greater

rigidity of the polymer chains of DMBP-TB, resulting in a higher energy barrier for hydroxide hopping, which in turn requires higher temperatures to undergo the thermal motions that are apparently necessary to form sufficiently overlapping hydration shells and to facilitate enhanced anion transport.

The performance and stability of the TB polymer-derived AEMs are all the more remarkable due to the simplicity of their preparation, which involves only two simple synthetic steps (TB polymerization and quaternization), from inexpensive starting materials. In contrast, current state-of-the-art AEM materials are prepared using multi-step procedures to provide relatively complex macromolecular structures that phase-separate into hydrophobic regions for stability and hydrophilic regions for anion transport.[16b,17] The design of such materials draws inspiration from the example of Nafion, in which phase separation is responsible for its excellent performance as a proton-exchange membrane (PEM). For the TB polymers, DMDPM-QTB and DMBP-QTB, the anion conducting pathways appear to be provided on a smaller scale by the inefficient packing of the polymer chains caused by the rigid V-shape of the quaternized TB unit. Analogous to gas permeability through polymers of intrinsic microporosity (PIMs), the transport of hydrated anions within the amorphous TB polymers will be facilitated by hopping between subnanometer free-volume voids between the polymer chains, although for the anions these voids will be occupied by water molecules to provide a sponge-like structure. Interestingly, the closely related ultra-rigid polymer with a higher degree of intrinsic microporosity (Trip-TB) performed relatively poorly due to excessive water uptake and chemical instability. In contrast, DMBP-TB, which is a rigid polymer that possesses some rotational freedom along its chain, provided DMBP-QTB having exceptional σ_{OH^-}. However, the highest σ_{OH^-} values were achieved only at elevated temperature, indicating that the enhanced anionic transport requires activation through thermally induced motion. The structural diversity offered by TB polymers[11] and the relative simplicity and broad applicability of the synthetic approach provide many opportunities for further optimization of their performance as AEMs. Investigations towards this objective are in progress.

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