

Electronic Supplemental Information: Radiation-grafted anion-exchange membranes: should crosslinking be introduced in the grafting or amination synthesis step?

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This ESI document (CC-BY) presents the results of screening experiments used to determine the best diamine to use in the main study. These results were generated in Dr Terry Willson's PhD project [Thesis can be downloaded from <https://epubs.surrey.ac.uk/846392/> (CC-BY-NC)]

Summary experimental description for diamine screening (full details can be found in the above thesis):

The RG-AEMs were made from 50 μm ETFE films that were electron-beamed to a total absorbed dose = 70 kGy and grafted with vinylbenzyl chloride (mixture of *meta*- and *para*-isomers, 97%, Sigma-Aldrich). The poly(VBC)-grafted membranes were then submerged in aqueous (50 vol%) solutions containing the following diamines: *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *N,N,N',N'*-tetramethylpropane-1,3-diamine (TMPDA), and *N,N,N',N'*-tetramethylhexane-1,6-diamine (TMHDA). In the case of 1,4-diazabicyclo[2.2.2]octane (DABCO), amination was carried out using an aqueous (1 mol dm⁻³) solution. These diamines were selected due to their commercial availability and non-excessive cost. The specific aminations were conducted under reflux at 80°C for 48 h. The resultant RG-AEMs (in the Cl⁻ form) were washed several times in ultra-pure water (UPW) then boiled in UPW for 1 h to remove any excess amines. Finally, RG-AEMs were stored under ultra-pure DI water until required. The quaternary ion-exchange capacities (IEC_{quat}) of this batch of RG-AEMs were 1.35 \pm 0.25 meq g⁻¹.

Data and discussion

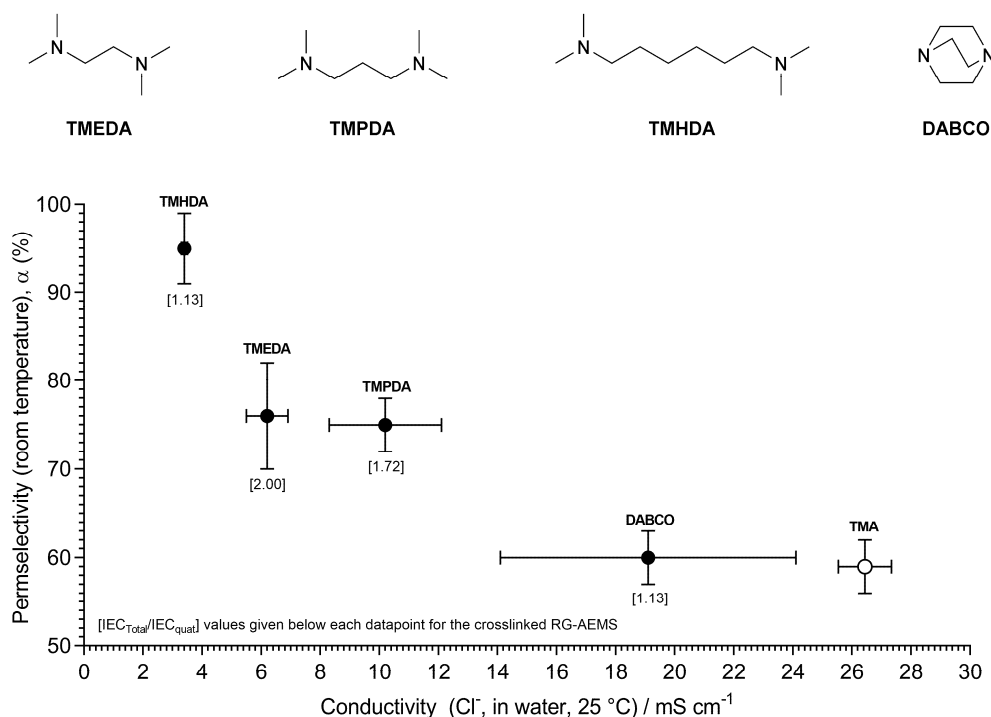


Figure ESI1 A comparison of the permselectivities and Cl⁻ conductivities of the RG-AEMs made using four diamines. A trimethylammonium (TMA) benchmark RG-AEM is also included. Values in [] indicate the ratio of total ion-exchange capacity (IEC_{Total}) normalised to quaternary ion-exchange capacity (IEC_{Quat}): a ratio = 1 means the diamine reaction is fully crosslinking (diamine has reacted via both nitrogen atoms), a ratio = 2 means the diamine has reacted *via* only a single nitrogen atom (non-crosslinking), while numbers in between indicate intermediate levels of crosslinking.

The data in Figure ESI1 shows that TMEDA and TMPDA react in a predominantly non-crosslinking way. The RG-AEM made with DABCO had the highest conductivity but the lowest permselectivity. Therefore, TMHDA was selected for use in the main study due to the desired effect on permselectivity (target $\alpha > 90\%$).