Studies into the alkali stabilities of fully hydrated anion-exchange membrane head-groups

Sam Murphy and John R. Varcoe

Department of Chemistry
University of Surrey
Guildford GU2 7XH, United Kingdom

Alkaline polymer electrolyte fuel cells (APEFCs) are being investigated due to the promise of the application of of non-precious-metal catalysts [1]. A major problem is the lack of satisfactory alkali stabilities of the anion-exchange membrane (AEM) head-groups. These head-groups are very susceptible to attack by the very hydroxide (OH^-) anions required to be present for high conductivity and operation in APEFCs [2]. Quaternary ammonium head-group degradation is most severe when the polymer electrolytes are less than fully hydrated (as the OH^- anions are more nucleophilic when less hydrated).

This presentation will detail the development of various spectroscopic methods for studying the stability of AEMs and model small molecules containing various anion-exchange head-groups. This is a study of the stability of these head-groups in a highly mobile and hydrated environment.

Head-groups will include the benchmark quaternary ammonium as well as those based on imidazoliums [3], DABCO [4], quinuclidine [5] and various aliphatic diamines including tetramethylhexane diamines. The techniques used include FT-Raman spectroscopy [6] and nuclear magnetic resonance spectroscopy (solid state and high resolution solution-based) [7].

Results to date indicate the benzyl-based imidazolium head-groups are less stable than benzyltrimethyl-ammonium (see Figures 1 and 2) in aqueous KOH (1 mol dm^{-3}) at the test temperatures of 60°C. The various head-groups also appear to be more stable in aqueous carbonate and bicarbonate solutions (1 mol dm^{-3}) than compared with aqueous hydroxide solutions. This is in support of studies by others (e.g. [8]).

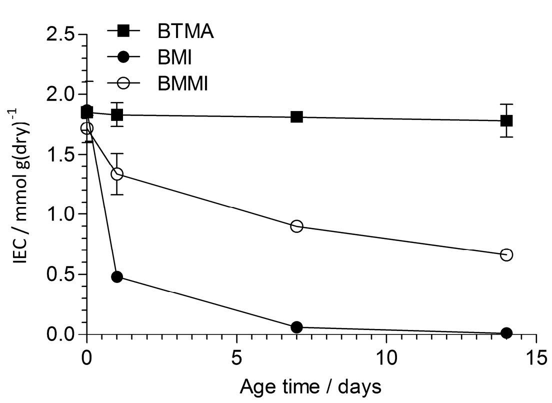

Figure 1: The change in ion-exchange capacity with alkali ageing time (aqueous KOH, 1 mol dm^{-3}, 60°C) of radiation-grafted membranes containing 1-benzyl-3-methylimidazolium [BMI], 1-benzyl-2,3-dimethylimidazolium [BMMI] and benzyltrimethylammonium [BTMA] head-groups.

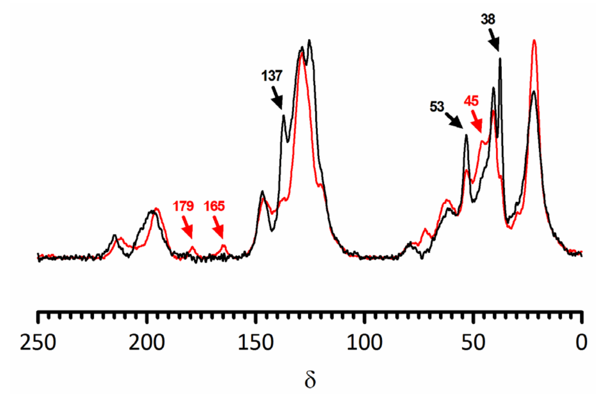

Figure 2: The solid state ^{13}C NMR spectra (in ppm vs. tetramethylsilane shift reference) of a radiation grafted membrane containing 1-benzyl-3-methylimidazolium head-groups before (black) and after (red) alkali ageing (same ageing conditions as in Figure 1). The red labels indicate new spectral features on alkali ageing, whilst the black labels indicate spectral features that changed significantly on ageing.

The presentation at the 223rd ECS (May 2013) meeting in Toronto will build on these results with new head-group chemistries. There will be significant comment on the methodologies that should be used to study the alkali stabilities of both membrane and model molecule bound head-groups; this will include stability testing of AEMs in the alkali form but in the absence of excess alkali (*i.e.* AEMs [in OH^- forms] aged in water rather than aqueous KOH solutions). The model small molecule work facilities the elucidation of the degradation pathways.

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