An alkaline polymer electrochemical interface: a breakthrough in application of alkaline anion-exchange membranes in fuel cells

John R. Varcoe,* Robert C. T. Slade and Eric Lam How Yee

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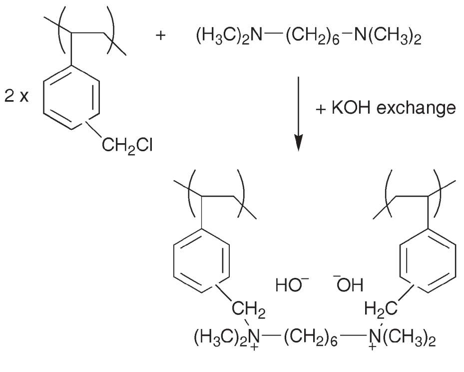
A novel alkaline polymer has been developed as an interfacial material for use in the preparation of metal-cation-free alkaline membrane electrode assemblies (MEAs) for all-solid-state alkaline fuel cells (AFCs) with long-term performance stability.

There is now considerable interest in the application of alkaline anion-exchange membranes (AAEMs, OH^--conducting membranes) in fuel cells. The advantages and disadvantages of this have been detailed in recent reviews,[1] a summary of the benefits being: (1) enhanced electrokinetics with the potential for the use of non-noble metal catalysts, such as Ag,[2] and higher energy density fuels compared to methanol, such as ethylene glycol;[2] (2) lowered alcohol permeability;[3] and (3) improved water management.[1] The major inhibitor to the successful application of AAEMs in fuel cells is the current lack of an alkaline analogue to the commercially available Nafion® proton-exchange polymer dispersions that are used in producing the high performance membrane electrode assemblies (MEAs) found in current state-of-the-art proton-exchange membrane fuel cells. Hence, non-ideal strategies, such as adding KOH into the alcohol fuel supply and electrode structures or use of Nafion® dispersions,[2–4] have been implemented. It is essential that no metal cations (*e.g.* K^+, Na^+) are present in alkaline fuel cells in which CO_2 is supplied to or generated at the electrodes, otherwise undesirable carbonate precipitation will occur, a major problem with traditional aqueous KOH electrolyte AFCs.[5]

The breakthrough reported in this communication is the successful development of a cross-linked (OH^--exchanging but water insoluble) alkaline interface polymer (Scheme 1) that allows the preparation of AAEM-MEAs† that do not contain any M^{n+} ions: the counter ions (quaternary ammonium groups) to the OH^- conduction species are bound to the polymer backbone in the same manner as the counter ions (SO_3^- groups) are bound to the polymer backbone in commercial H^+-conducting polymers (*e.g.* Nafion®). This work follows on from the extensive development of state-of-the-art conductive, chemically and thermally stable quaternary-ammonium-containing AAEMs by the authors.[6]‡ *N*,*N*,*N*′,*N*′-tetramethylhexane-1,6-diamine was selected as the amination/cross-linking agent due to recent reports that cross-linked polymers synthesised using this diamine exhibited high stability towards alkali.[7] Reaction between the diamine and poly(vinylbenzyl chloride) was confirmed using Raman spectroscopy.§



Scheme 1 Cross-linked alkaline interface polymer synthesis.

Fig. 1 compares the H_2/O_2 fuel cell performance curves obtained with AAEM-MEAs both with and without the alkaline interface. It was seen that there was a substantial increase in the peak power density at 50 °C (from 1.6 to 55 mW cm^{-2}) on simply adding the interface polymer. It should be noted that the electrodes used for the MEA without interface polymer contained 4 mg cm^{-2} Pt black and not the 0.5 mg cm^{-2} Pt/C used for the MEA with the interface, as the performances were otherwise too poor to measure. As a control experiment, an AAEM-MEA was fabricated with electrodes treated with diamine and KOH only, *i.e.* without added poly(vinylbenzyl chloride); this resulted in no increase in performance. The above result compares well with the 42 mW cm^{-2} peak power density obtained at 25 °C by Agel *et al.*,[4] who used a KOH-based MEA alkaline interface with an AAEM that exhibited sufficient conductivity only with the pre-adsorption of KOH.

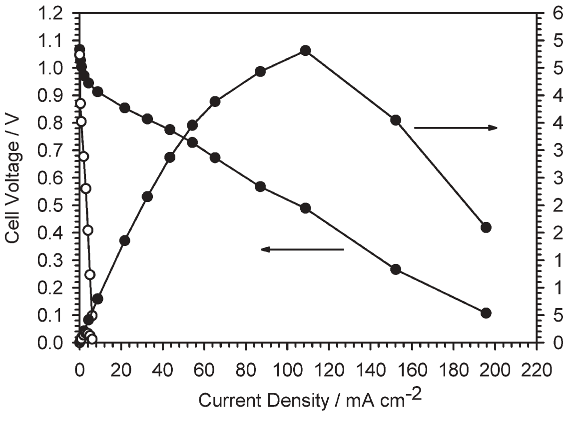


Fig. 1 Fuel cell test data obtained with AAEM-MEAs with 0.5 mg cm^{-2} Pt/C (20 wt%) electrodes coated with the alkaline interface polymer (●) and with 4 mg cm^{-2} Pt black electrodes without the interface (○). Test conditions: 50 °C, 2 dm^3 min^{-1} RH = 100%, O_2 and H_2 gas flows at the cathode and anode respectively, no added back pressures.

Chemistry (C4), The University of Surrey, Guildford, UK GU2 7XH.
E-mail: j.varcoe@surrey.ac.uk; Fax: +44 1483 686851;
Tel: +44 1483 682616

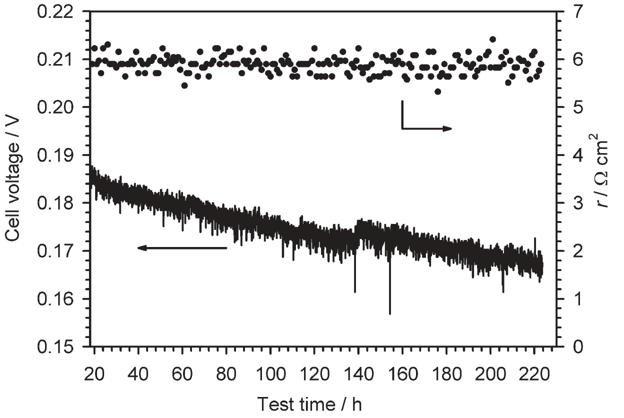


Fig. 2 Medium-term test with an AAEM-MEA (4 mg cm^{-2} $PtRu_{ox}$ anode and 4 mg cm^{-2} Pt black cathode both with the alkaline interface). Test conditions: 50 °C, 0.1 A discharge, cathode: 2 dm^3 min^{-1} air (RH = 100%), anode: methanol (2 mol dm^{-3}, 2 cm^3 min^{-1}), no back pressures.

The work reported above constitutes the first attempt at an all-solid-state AAEM-MEA and produced a performance that was within 1 order of magnitude of the MEA-containing proton-exchange materials that have been optimised over decades. A peak power density of 480 mW cm^{-2} was obtained when a traditional Nafion115¶-containing MEA (with the application of dispersed Nafion onto 4 mg cm^{-2} Pt black electrodes at the same loading as that used for the AAEM-MEA) was tested under the same conditions. Internal resistance measured throughout fuel cell testing (standard current pulse) with the Nafion115-MEA (0.4 Ω cm^2) was lower than that found with the AAEM-MEA (1.5 Ω cm^2), which was a contributing factor towards the lower power performance of the latter. Further noteworthy points are that (1) the AAEM used, (2) the level of loading of the alkaline interface polymer, and (3) the electrode fabrication methodology are all far from optimised; a study into these factors is now being undertaken, and higher performances are anticipated in the future.

An AAEM-MEA was tested in methanol/O_2 mode (direct methanol fuel cell, DMFC) under the same test conditions as the H_2/O_2 test presented in Fig. 1, except that the H_2 anode supply was replaced with preheated aqueous methanol (50 °C, 2 mol dm^{-3}, 10 cm^3 min^{-1}, no back pressure). This gave a peak power density of 0.9 mW cm^{-2}. This compares poorly to recent results published by Yu and Scott using a commercial AAEM (Morgane®-ADP, Solvay S.A., Belgium) where peak power densities of 18 mW cm^{-2} were obtained;[8] these performances were, however, obtained with KOH added to the aqueous methanol anode fuel supply. As mentioned above, this neutralises any advantage with replacing aqueous KOH electrolyte with AAEMs in AFCs; the absence of mobile metal cations eliminates problematic, potentially performance destroying, carbonate precipitation in the electrode structures.[5]

Fig. 2 presents a 233 h durability test, with the same AAEM-MEA, tested in methanol/air mode (CO_2 supplied to the cathode as a component of air and generated at the anode from electro-oxidation of methanol). The results constitute a breakthrough in AFC technology. The cell voltage stabilised to a degradation rate of 95 ± 10 μV h^{-1} (with no associated increase in cell area resistance—measured to be 5.9 ± 0.2 Ω cm^2 throughout the test); this represents a respectable performance degradation for any type of DMFC. These performance data indicate that the interface polymer is cross-linked. After this 233 h test, the methanol/O_2 performance was re-evaluated, and the peak power density was observed to have increased to 1.1 mW cm^{-2}; this clearly indicates that performance was recoverable. The ion-exchange capacity of the membrane after the 233 h test had reduced by less than 5%. In contrast, the performance of a KOH electrolyte AFC (6 mol dm^{-3}) degraded rapidly over the course of 70 h at 60 °C and 94 h at 30 °C, due to carbonate precipitation at the anode, when fuelled with methanol.[9] The above observations demonstrate that elimination of M^{n+} cations in such systems minimises performance losses due to carbonation, thereby allowing alcohols to be used in AFCs. This is contrary to current wisdom and fully validates the innovative approach outlined in this article. Future work, as well as the MEA optimisation mentioned above, will include the evaluation of Pd-, Ag- and Au-containing electrodes in AAEM-MEAs.

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Notes and references

† Poly(vinylbenzyl chloride) (Aldrich, *meta-/para-* mixture) was dissolved in ethyl acetate (50 mg cm^{-3}) and sprayed to a loading of 0.97 ± 0.05 mg cm^{-2} onto the catalysed side of standard commercial carbon-cloth electrodes (E-Tek, either 0.5 mg cm^{-2} Pt/C (20 wt%), 4 mg cm^{-2} $PtRu_{ox}$, or 4 mg cm^{-2} Pt black). The polymer-treated electrode was then immersed in *N,N,N′,N′*-tetramethylhexane-1,6-diamine (Acros Organics, toxic) for 24 h, washed thoroughly with water, soaked in aqueous KOH (1 mol dm^{-3}) for 1 h to convert the polymer interface to the OH^- form, and finally washed thoroughly with water to remove any residual KOH. The electrodes were pressed onto the alkaline polymer (freshly converted to the OH^--form) at 100 °C for 3 min at 120 kgf cm^{-2}.

‡ The AAEM used in this study had the following relevant properties: 1.14 ± 0.02 × 10^{-3} mol(OH^-) g^{-1}(dry membrane); [OH^-] = 1.21 ± 0.05 mol dm^{-3}, a density of 1.36 ± 0.04 g cm^{-3}, a water content of 15 ± 2 H_2O molecules/OH^- ion, a thickness of 153 ± 4 μm when fully hydrated and a thickness of 133 ± 4 μm when fully dehydrated. The conductivity at 30 °C and RH = 100% was determined to be 0.0092 ± 0.0005 S cm^{-1} using standard electrochemical impedance spectroscopic techniques.[6]

§ The CH_2Cl deformation band at 1680 cm^{-1} in the Raman spectrum of poly(vinylbenzyl chloride) vanishes, whilst new bands at 1451 and 757 cm^{-1} appear in the spectrum of the final cross-linked polymer; these bands are reported for NCH_3-functionalised quaternary-ammonium-containing materials[6] and are also present in the spectrum of poly(vinylbenzyltrimethylammonium chloride). The intense bands at 2765 and 2729 cm^{-1} present in the spectrum of the diamine are not visible in the spectrum of the final materials, confirming no residual diamine.

¶ Nafion115 (DuPont): 0.92 mol(H^+) g^{-1}(dry membrane); 153 μm thickness and 23 H_2O molecules/H^+ ions when fully hydrated; conductivity of 0.064 S cm^{-2} at 30 °C and RH = 100%.

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