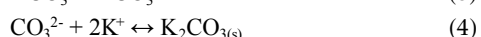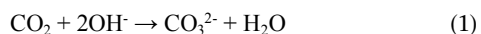# The Chalkboard

Anion Exchange Membrane Fuel Cells

by Christopher G. Arges, Vijay Ramani, and Peter N. Pintauro

Proton exchange membrane fuel cells (PEMFCs) are currently capable of providing power for a variety of applications, ranging from automotive transportation to portable electronics to military devices. The widespread commercialization of PEMFCs, however, remains a challenge due to cost, lifetime, and fueling issues.[1,2] The need for precious metal catalyst electrodes in PEMFCs is of concern because of uncertainties regarding the future availability and price of platinum group metals (PGMs), should PEM fuel cells see widespread use. It is not at all certain that that there is enough Pt in the world today to sustain a sizable fraction of autos in the U.S. being powered by PEMFCs.

Anion exchange membrane fuel cells (AEMFCs) are, in principle, a viable alternative to PEMFCs and are currently garnering renewed attention. In an AEMFC, an anion exchange membrane (AEM) conducts hydroxide (or carbonate) anions (as opposed to protons) during current flow, which results in several advantages. (1.) The oxygen reduction reaction (ORR) is much more facile in alkaline environments than in acidic environments.[3] This could potentially facilitate the use of less expensive non-PGM catalysts with high stability in alkaline environments. (2.) The electro-oxidation kinetics for many liquid fuels (including non-conventional choices of importance to the military, such as sodium borohydride) are enhanced in an alkaline environment. (3.) The electro-osmotic drag associated with ion transport opposes the crossover of liquid fuel in AEMFCs, thereby permitting the use of more concentrated liquid fuels. This is an advantage for portable applications. (4.) The flexibility in terms of fuel and ORR catalyst choice also expands the parameter space for the discovery of highly selective catalysts that are tolerant to crossover fuel. These potential advantages make AEMFCs an attractive future proposition.

Alkaline fuel cells were first developed in the 1930s by F. T. Bacon, thus they pre-date PEM fuel cells and represent one of the oldest fuel cell types. Early alkaline fuel cells operated with H_2 as the fuel at a temperature between 50 and 200°C and employed a liquid electrolyte (*e.g.*, an aqueous solution of KOH). NASA used such fuel cells in the 1960s to power Apollo space missions. The technology, however, has suffered from problems arising from the use of liquid (aqueous) electrolytes; in particular the inevitable shunt currents and poisoning by carbon dioxide which leads to the formation of carbonate precipitates[3] in the liquid electrolyte. The chemistry behind the carbonate precipitation problem is presented below.
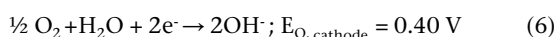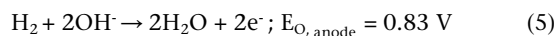
$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \qquad (1)$$
$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (2)$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (3)$$
$$CO_3^{2-} + 2K^+ \leftrightarrow K_2CO_{3(s)} \qquad (4)$$

The strongly alkaline electrolytes absorb even the smallest amount of CO_2, which in turn eventually reduces the conductivity of the electrolyte. Consequently pure hydrogen (rather than an impure hydrogen stream containing CO_2) and highly purified oxygen (rather than air) must be used as the fuel and oxidant feeds. The use of such high purity oxygen, in particular, increases significantly the cost of generating electricity with a liquid electrolyte alkaline fuel cell.
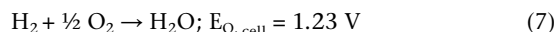
Today, researchers have moved to polymeric anion exchange membranes (AEMs) as the hydroxide transport medium in an alkaline fuel cell. In the AEM, cationic moieties are fixed to polymer chains (and are not freely mobile as in a liquid electrolyte). This prevents the formation of carbonate precipitates (*i.e.*, there is no liquid-phase dissociated cation which can react with carbonate anions to form insoluble species like K_2CO_3). AEMs, however, suffer from low ionic conductivity and poor chemical stability, especially at the cationic site.[3,4] Additionally, most anion exchange membrane polymers have poor solubility in low boiling, inexpensive solvents, like the alcohol/water solvents used with proton conducting perfluorosulfonic acid polymers in PEM fuel cells. This makes for more complicated and less environmentally friendly membrane fabrication schemes. It also complicates the process of incorporating an anion exchange polymer binder into the electrode layers of an AEMFC membrane-electrode-assembly (MEA). Thus, the preparation of catalyst coated membranes for AEMFCs lags far behind similar work with PEMFCs.[5] This Chalkboard article will briefly outline AEMFC operation, AEM chemistry, and key challenges to this technology.

Overview of AEMFC Operation

For a traditional AEMFC with hydrogen fuel and air/oxygen as the oxidant, the half cell and overall chemical reactions are as follows:[3]

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-\,; E_{O,\,anode} = 0.83 \text{ V} \qquad (5)$$

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-\,; E_{O,\,cathode} = 0.40 \text{ V} \qquad (6)$$

Overall:

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O\,; E_{O,\,cell} = 1.23 \text{ V} \qquad (7)$$

In an AEMFC, hydroxide ions are generated during electrochemical oxygen reduction at the cathode. They are transported from the cathode to the anode through the anion conducting (but electronically insulating) polymer electrolyte, wherein they combine with hydrogen to form water. The electrons generated during H_2 oxidation pass through the external circuit to the cathode, where they participate in the electrochemical reduction of oxygen to produce OH^-. Note that in practice, the ideal thermodynamic cell voltage of 1.23 V (at standard conditions) is not realized even at open circuit (zero current) due to myriad irreversibilities that arise during AEMFC operation. The phenomenological sources of irreversibility are very similar to those in PEMFCs and include oxygen and water activities that are less than unity, and gas crossover at open circuit leading to mixed potentials, and activation, ohmic, and mass transfer losses (overpotentials)
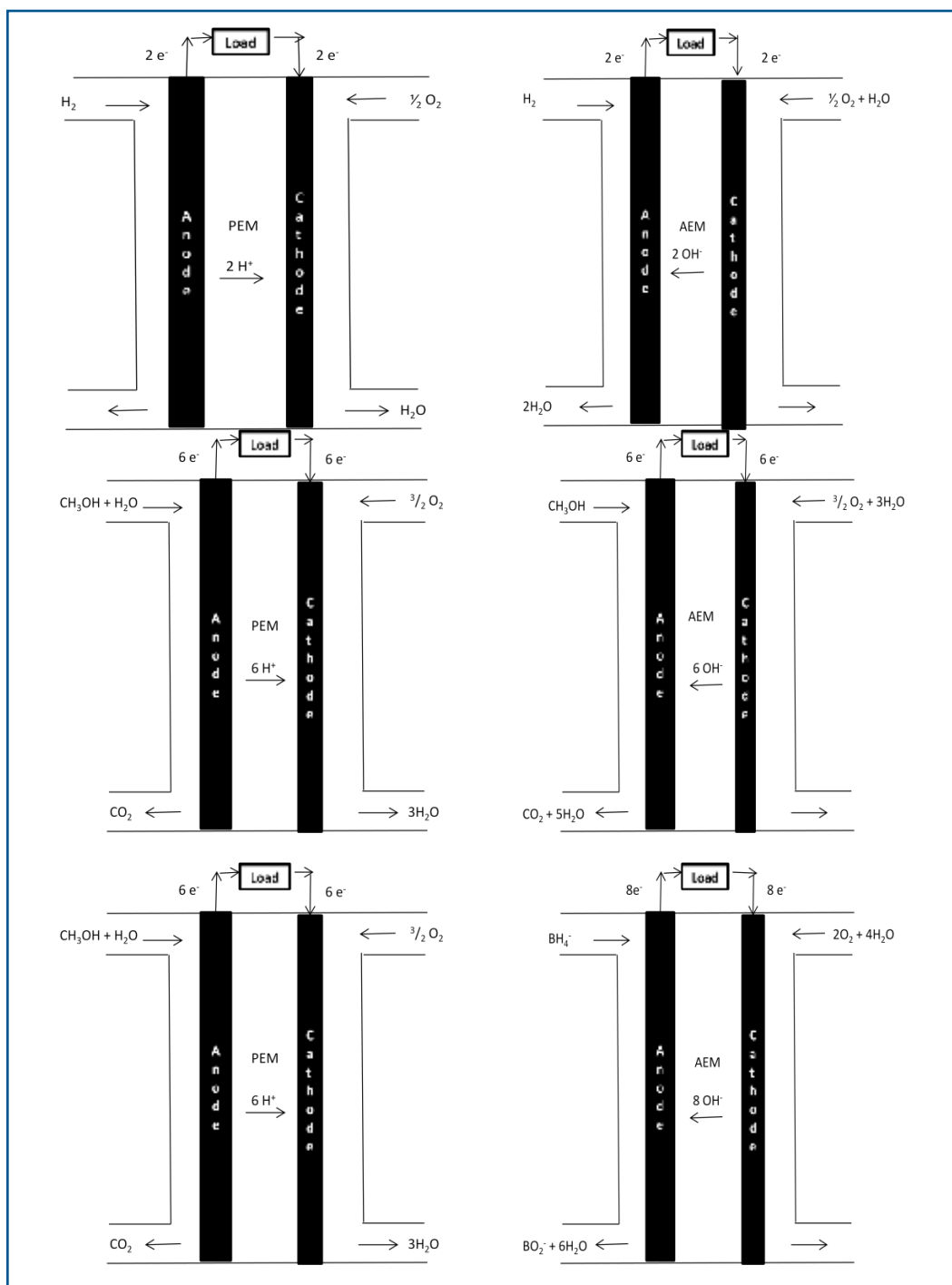
Fig. 1. *Comparison of AEM and PEM fuel cell configurations for hydrogen, methanol, and sodium borohydride as fuel.*

another, to the properties of the final membrane, and to the eventual large-scale commercial process for membrane manufacturing. In general, fuel cell membranes must meet stringent performance, durability, and cost targets. More specifically, as shown in Fig. 2, the requirements for the successful commercial production of an alkaline fuel cell membrane include a robust synthetic route with the proper selection and positioning of cationic ion-exchange groups on the polymer, control of the membrane morphology to improve mechanical properties, scalability, and the use of low cost materials and processing methods. Membranes are typically composed of a polymer backbone onto which fixed cationic sites are tethered. For example, one can functionalize polysulfone via chloromethylation followed by reaction with an amine (quaternization) or phosphine to yield a quaternary ammonium or phosphonium salt. The salt form of the membrane is readily alkalinized by treatment with KOH to yield a hydroxide ion conducting AEM. As an example, Fig. 3 shows the reaction scheme for converting Udel® polysulfone (from Solvay Advanced Polymers LLC) into an anion-exchange membrane polymer.

The first and foremost challenge for polymer chemists, membrane scientists, and electrochemists is to fabricate anion-exchange membranes with a high OH^- ion conductivity and good mechanical properties. Anion-exchange groups do not strongly dissociate (as do SO_3H groups in cation-exchange membranes like Nafion®) and the inherent electrochemical mobility of OH^- in water is much lower than that of a proton. Thus, it is very difficult for the ionic (hydroxide) conductivity of AEMs to approach that of typical/commercial PEMs. While AEM ionic conductivity can be enhanced by increasing the number of cationic sites, *i.e.* by increasing the polymer's ion exchange capacity (IEC), this approach is limited due to the concomitant deterioration in AEM mechanical properties with increasing fixed charge concentration; *i.e.*, excessive swelling and the loss of mechanical properties when the membranes are fully hydrated and brittleness when the films are partially hydrated or dry. Typical fuel cell conductivity *vs.* ion-exchange capacity data (in water at 25°C) are shown in Fig. 4 for a block copolymer anion-exchange membrane

during current flow. Figure 1 contrasts AEM and PEM fuel cell operation with different fuels (H_2 gas, liquid methanol, and sodium borohydride). Table I presents a list of possible fuels for AEMFCs with their standard thermodynamic cell voltages (using an air cathode) and their energy densities.

Anion-Exchange Membrane Chemistry and Associated Challenges

Perhaps the single greatest obstacle in developing a commercially viable AEMFC is the anion-exchange membrane. The method and materials used to fabricate an anion-exchange membrane for alkaline fuel cells are intimately linked to one

based on xylylene ionenes.[5] The conductivities are quite low, considering the high polymer ion-exchange capacity. Additionally, excessive membrane swelling for IECs > 2.2 mmol/g causes the conductivity to drop with increasing fixed charge concentration (swelling reduces the effective membrane-phase concentration of fixed charges, leading to a drop in conductivity).

It has been well documented that AEMs also suffer from poor chemical stability (ironically in alkaline environments).[3,4] Chemical degradation of AEMs stems largely from nucleophilic attack on the cationic fixed charged sites by hydroxide ions. Consequences of this degradation mechanism are a loss in the number of ion-exchange groups, with a subsequent decrease in OH- ion conductivity. A key mode of degradation for AEMs is the Hoffman elimination reaction, wherein hydroxide ions attack a hydrogen atom on the beta carbon relative to the cation. In this degradation mechanism, a double bond forms between the alpha and beta carbons, resulting in the cation being released (See Fig. 5). Another mode of polymer degradation is direct nucleophilic displacement at the cation site, which can occur by two possible reaction pathways in quaternary ammonium fixed-charge site membrane (see Figs. 6 and 7). Here, in the absence of beta hydrogens, hydroxide ions attack either a methyl group on the quaternary ammonium moieties and form an alcohol or attack the C-C bond between the alpha and beta carbons to cleave the cation site.[3,4] More information on these and other degradation modes are available in the literature.[6 (a-d)] There are on-going efforts to better understand[6 (c,d)] degradation mechanisms and either modify or re-design the cation sites in AEMs.[7]

The development of methods and materials for AEMFC membrane-electrode-assembly (MEA) fabrication lag far behind similar work for proton exchange membrane fuel cells. Difficulties lie in the inherently low hydroxide conductivity and poor durability of anion-exchange polymer binders, the absence of suitable low boiling-point, water-soluble organic solvents for catalyst ink preparation, and the absence of fast and efficient membrane/electrode attachment schemes (*i.e.*, techniques analogous to the hot-pressing and decal methods used for proton exchange membrane fuel cell MEAs). Most studies in the literature use of Pt catalysts in AEMFC prototypes, as opposed to non-noble metal catalysts, which negates a prime advantage of alkaline fuel cells as compared to PEM devices. Thus, there remains a need for further AEMFC catalyst development and a need to show prototype operational

AEMFCs that are totally free of precious metals. Two recent papers illustrate the challenges facing MEA fabrication scientists and engineers who are searching for materials and processing schemes that will boost AEMFC power outputs. In one paper,[8] Y. Yan and coworkers utilize a methanol-soluble quaternary phosphonium containing anion-exchange polymer as the electrode binder in an AEMFC, where Pt-black was used as the anode and cathode electrocatalysts and a Fuma-Tech GmbH anion-exchange membrane (0.017 S/cm conductivity in water at 20°C) was used to prepare MEAs. A power density of 138 mW/cm² was achieved at 70°C with pressurized H_2 and O_2 feed. In another paper,[9] L. Zhuang, *et al.*, fabricated an AEMFC membrane-electrode-assembly with a Ag anode and a Cr-decorated Ni cathode (*i.e.*, with no Pt), where a quaternary ammonium polysulfone was used as the membrane and electrode binder. For H_2 and O_2 feeds at a pressure of 1.3 atm. and an operating temperature of 60°C, a maximum power density of 50 mW/cm² was reported. The power densities reported in these two articles are far below those that are typically achieved in a PEM fuel cell with hydrogen and air feeds at Pt/C electrodes (600-700 mW/cm² at 60°C). Also, the use of O_2 for the cathode feed is unrealistic for consumer applications.

Table I. Fuels for AEM fuel cells with standard thermodynamic voltages and energy densities.

Fuel	Standard Thermodynamic Voltage, $E_{0, cell}$, [V]	Energy Density [kWh/kg]	References
Hydrogen	1.23	39.0	[3]
Methanol	1.21	6.1	[3]
Ethanol	1.15	8.0	[3]
Propanol	1.07	8.6	[3]
Ethylene Glycol	1.22	5.3	[3]
Sodium Borohydride	1.24	9.3	[10]

Alkaline Fuel Cell Membranes

Robust Synthetic Route
• Highly specific chemistry
• Ability to add different cationic groups
• Mild reaction conditions

Selection of Fixed-Charge-Site Cation
• High cation stability
• High fixed-cation concentration in the membrane
• Appropriate cation placement in macromolecular structure

Control of Membrane Morphology
• Use of block or segmented copolymers; polymer croslinking
• Controllable nano-phase separated morphology
• Crystallizable non-polar segments

Scalability
• Inexpensive starting materials
• Simple reaction schemes
• Solution casting of membranes using standard solvents/equipment

Fig. 2. *General requirements for the successful production of alkaline fuel cell membranes.*

Summary and Outlook

Theoretically, AEMFCs can operate on a variety of fuels and generate high power densities at moderate operating temperatures. The real advantage (albeit not currently realized in practice) of AEMFCs vis-à-vis PEM fuel cells is the absence of expensive noble metal catalysts in the electrodes. AEMFCs have their own set of challenges, as related to materials and processing schemes, which require innovative engineering solutions. Key among these are the conductivity and durability of the anion-exchange membrane, the identification of suitable OH⁻ ion conductive polymers for anode and cathode binders, and the identification/optimization of membrane-electrode-assembly preparation methods. Recently, there has been a surge in alkaline fuel cell research activities and interest. Many researchers are switching their research outlook from an exclusive focus on PEMs/PEMFCs to one that includes (at a significant level of effort) AEM and AEMFCs. Progress is being made, research funding for AEMFCs is seeing an upward trend, and more papers on the subject are being published. The very positive developments over the past ten years resulting in improved PEMFC performance and durability with lower manufacturing costs bode well for similar progress on the AEMFC front, especially given the increasing commitment to this technology that is emerging.

Fig. 3. *The chemical reaction steps to convert a polysulfone to an anion-exchange membrane polymer.*

About the Authors

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Vijay K. Ramani is an Assistant Professor of Chemical Engineering in the Department of Chemical and Biological Engineering at Illinois Institute of Technology, Chicago. His research interests lie in the broad area of electrochemical engineering, with an emphasis on materials for electrochemical energy conversion and storage. NSF, ONR, and DOE currently fund his research. He is the recipient of a 2009 NSF-CAREER award as well as a 2010 ONR-Young Investigator Award (ONR-YIP). Ramani has a PhD from the University of Connecticut, Storrs, and a BE from Annamalai University, India, both in chemical engineering. He may be reached at ramani@iit.edu.
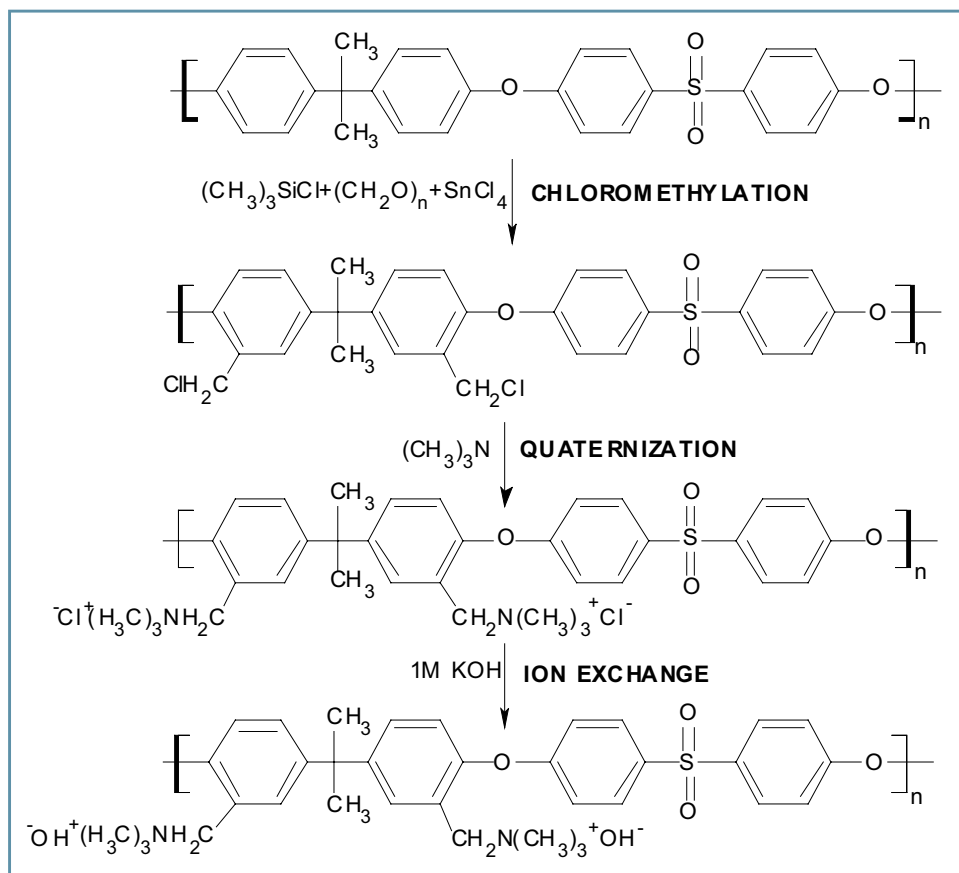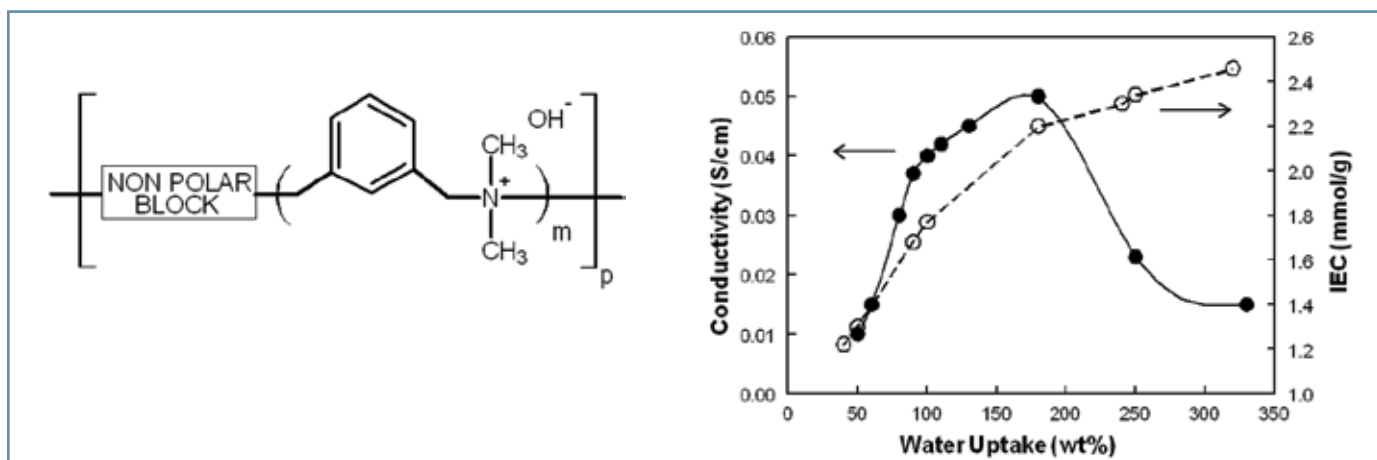

Fig. 4. *General chemical structure of a block copolymer based on xylylene ionenes (left) and typical variations in OH⁻ ion conductivity and water uptake with membrane ion-exchange capacity (from Ref. 5).*
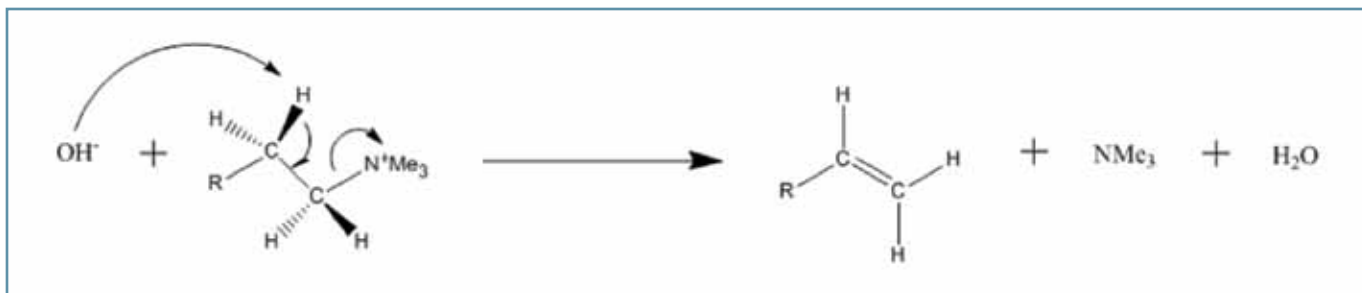
Fig. 5. *AEM degradation mechanism: the Hoffman elimination reaction.*
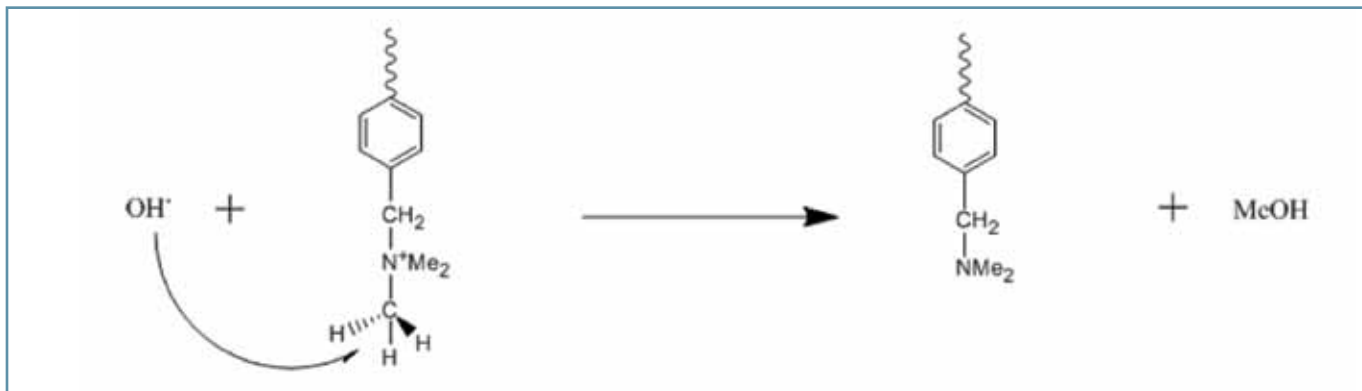

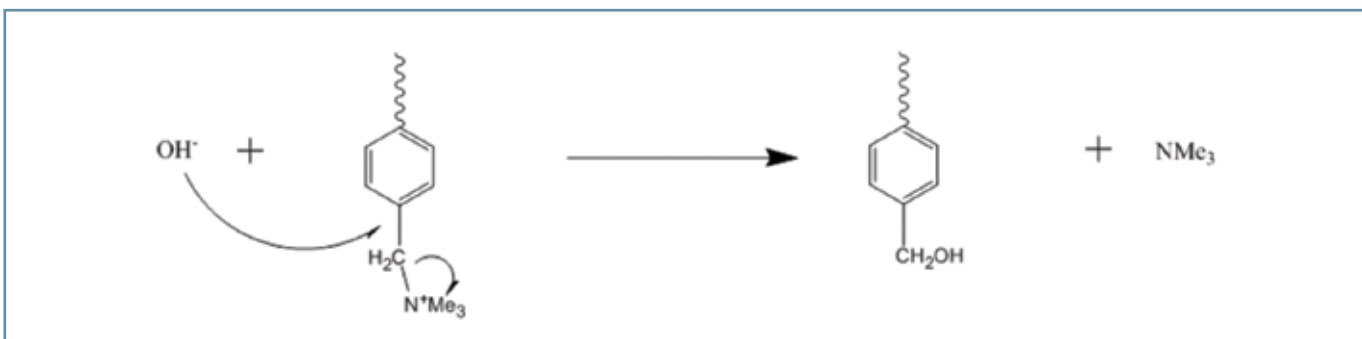**Fig. 6.** *AEM degradation mechanism: direct nucleophilic substitution – pathway 1.*

Fig. 7. *AEM degradation mechanism: direct nucleophilic substitution – pathway 2.*

Peter N. Pintauro is the H. Eugene McBrayer Professor of Chemical Engineering and Chair of the Department of Chemical and Biomolecular Engineering at Vanderbilt University. His research interests include new ion conducting membranes for fuel cells, development of space-charge models for ion uptake and transport in ion-exchange membranes, and organic electrochemical synthesis. He has BS and MS degrees from the University of Pennsylvania and a PhD from UCLA, all in chemical engineering. He may be reached at peter.pintauro@vanderbilt.edu.

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