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The critical relation between chemical stability of cations and water in anion exchange membrane fuel cells environment

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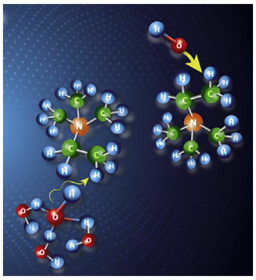
HIGHLIGHTS

- Water-free *ex-situ* stability test simulates the environment of AEMFCs in operation.
- Water/hydroxide has a critical influence on stability of quaternary ammonium groups.
- MD show shielding effect of water on the hydroxide, reducing its nucleophilicity.
- Very low hydration levels at cathode limits lifetime of AEMFCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Anion exchange membrane fuel cells can potentially revolutionize energy storage and delivery; however, their commercial development is hampered by a significant technological impedance: the chemical decomposition of the anion exchange membranes during operation. The hydroxide anions, while transported from the cathode to the anode, attack the positively charged functional groups in the polymer membrane, neutralizing it and suppressing its anion-conducting capability. In recent years, several new quaternary ammonium salts have been proposed to address this challenge, but while they perform well in *ex-situ* chemical studies, their performance is very limited in real fuel cell studies. Here, we use experimental work, corroborated by molecular dynamics modeling to show that water concentration in the environment of the hydroxide anion, as well as temperature, significantly impact its reactivity. We compare different quaternary ammonium salts that have been previously studied and test their stabilities in the presence of relatively low hydroxide concentration in the presence of different amounts of solvating water molecules, as well as different temperatures. Remarkably, with the right amount of water and at low enough temperatures, even quaternary ammonium salts which are considered "unstable", present significantly improved lifetime.

1. Introduction

Hydrogen based fuel cells (FCs) have been suggested as potential power sources for clean transportation, offering direct conversion of chemical to electrical energy [1]. Among the different types of

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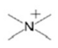
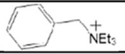
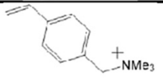
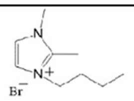
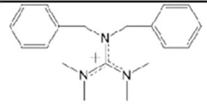
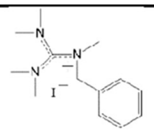
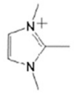
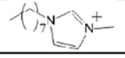
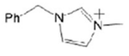
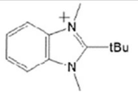
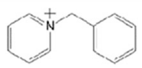
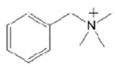
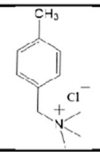
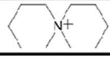
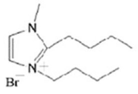
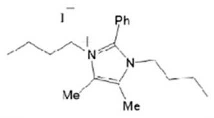
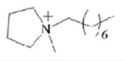
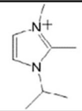
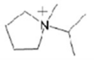
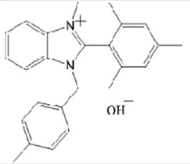
FCs, anion-exchange membrane fuel cells (AEMFCs) receive increased attention as they, in principle, eliminate the need of expansive platinum metal catalysts used in current acidic proton-exchange membrane fuel cells (PEMFCs). In the past five years, extensive research in hydrogen AEMFCs led to significant progress in this technology. A recent review summarized this historical progress and the state-of-the-art in cell performance of AEMFCs [2]. For instance, in the past years H_2-AEMFCs reached and exceeded peak power densities of 1 W cm^{-2} (at 0.50–0.70 V) and limiting current densities of above 2 A cm^{-2} [3,4]. These performance levels were achieved using Pt-based catalysts; however, excellent H_2-AEMFC performance was also obtained with Pd-decorated Ni or CeO_2 bifunctional anode catalysts and Ag-based cathode catalysts [5–7]. In spite of these achievements in performance, it has been shown that AEMFC performance stability is limited to less than 1000 h, and most commonly less than 300 h [2]. The key factor was pointed to be the restricted chemical stability of the anion exchange membranes (AEMs) in the AEMFC environment [2].

AEMs are polymeric electrolytes (also called ionomers) able to conduct anions, owing to the positively charged functional groups (FGs) present in the ionomeric structure. In recent years, different quaternary ammonium (QA) structures have been explored as potential FGs for AEMs [8,9]. Some of them showed excellent chemical stability towards hydroxide in laboratory experiments [10–13]; however, *ex-situ* stability tests might not adequately simulate the real fuel cell environment. When an AEMFC is in operation, hydroxide anions transported through the AEM from the cathode to the anode attack the positively charged FGs [8]. This leads to degradation of the FG and consequently, to a decrease in the AEM ability to conduct anions, which in turn reduces cell performance. As already mentioned, this limitation in the AEM durability is the key parameter defining the cell lifetime [14], and as clearly concluded in a recent review of the technology, performance stability is today the major remaining challenge in AEMFCs [2].

In order to overcome this challenge, considerable research has been directed to developing and identifying FGs that retain their anion conducting abilities in extreme alkaline conditions [15–35]. Table 1 summarizes some of these stability studies reported in the

Table 1
Selected QA *ex-situ* stability test results reported in the literature. ($^{\dagger}\lambda$ is calculated from the reported OH^- concentrations).

QA	C_{OH^-} [M]	λ†	T (°C)	t (h)	Deg. (%)	Ref.
	6	9	160	61.9	50	[23]
	10	6	160	19.5	50	
	6	9	160	0.68	50	[23]
	1	56	80	400	50	[36]
	2	28	80	432	3.2	[19]
	4	14	80	50	16.3	
	6	9	80	156	92.6	
	6	9	160	≈0	100	[23]
	1	56	60	48	81	[28]
	6	9	160	≈0	100	[23]
	6	9	60	≈0	100	[23]
	6	9	25	≈0	100	[23]
	0.5	111	RT	≈0	100	[36]
	6	9	25	≈0	100	[23]
	2	28	60	672	0	[31]
	2	28	120	672	13	
	2	28	80	2250	5	[37]
	6	9	160	4.18	50	[23]
	10	6	130	12.3	50	
	10	6	160	1.5	50	
	0.6	93	80	2887	50	[30]
	6	9	160	110	50	[23]
	1	56	80	240	0	[26]
	4	14	80	240	15.8	
	6	9	80	12	4.7	
	1	56	80	720	1	[29]
	2	28	80	720	3	
	5	11	80	720	7	
	1	56	80	168	4.3	[18]
	4	14	80	96	11.5	
	2	28	80	432	2.9	[19]
	4	14	80	50	1.6	
	6	9	80	156	22.5	
	1	56	80	168	4.9	[18]
	4	14	80	96	27.4	
	3	18.5	80	240	11	[33]

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