Are Radicals Formed During Anion-Exchange Membrane Fuel Cell Operation?

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ABSTRACT: In this paper we present a study on stable radicals and short-lived species generated in anion-exchange membrane (AEM) fuel cells (AEMFCs) during operation. The in situ measurements are performed with a micro-AEMFC inserted into a resonator of an electron paramagnetic resonance (EPR) spectrometer, which enables separate monitoring of radicals formed on the anode and cathode sides. The creation of radicals is monitored by the EPR spin trapping technique. For the first time, we clearly show the formation and presence of stable radicals in AEMs during and after long-term AEMFC operation. The main detected adducts during the operation of the micro-AEMFC are DMPO-OOH and DMPO-OH on the cathode side, and DMPO-H on the anode side. These results indicate that oxidative degradation involving radical reactions has to be taken into account when stability of AEMFCs is investigated.

In the recent decade, a significant amount of research has focused on the development of anion-exchange membrane (AEM) fuel cells (AEMFCs), as this technology exhibits faster oxygen reduction reaction (ORR) kinetics in the alkaline environment of the cell. Consequently, application of non-noble metal electrocatalysts, for example, based on transition-metal oxides of spinel structure, silver, and nickel as well as of low cost hydrocarbon-based membranes, is possible and, therefore, contributes directly to lower device costs and environmental benefits. However, for this technology to become a serious alternative to the current mainstream acidic fuel cell systems, it should overcome current limitations of performance stability. It has been recently shown that the chemical stability of the membrane during fuel cell operation in alkaline environments is a critical limitation of the AEMFC technology.

Among many different pathways of AEM degradation in alkaline media, the nucleophilic mechanism involving hydroxide ions (Scheme S1a,b) has been extensively investigated and described in the literature. The alkaline anion attacks are believed to be so severe in an AEMFC environment that degradation occurs over short time frames. Nucleophilic degradation occurs via ammonium group displacement, via either direct nucleophilic attack of OH− anions on nitrogen atoms in the ammonium group, resulting in alcohol departure or on the carbon atoms bonded with it, resulting in amine byproducts. In membranes with β-hydrogens present, degradation can also proceed by Hofmann elimination, resulting in formation of alkenes, tertiary amines, and water (Scheme S1c). Very recently, an outer sphere single-electron transfer (SET) was reported as a degradation mechanism of a novel carbazolium-based group, studied for their use as AEMs. The free radical pair generated from the SET reaction has been reported to provide sufficient driving force to initiate the degradation mechanism.

Despite significant impacts of nucleophilic degradation on ion-exchange capability and the anionic conductivity of investigated membranes, it is believed to affect only cationic sites of membrane polymers and thus cannot explain the reported loss in the mechanical strength of degraded AEMs. Such a phenomenon might be related to polymer backbone degradation caused by free radicals. This was widely described in the literature in the case of fuel cells using proton conducting membranes but barely mentioned for AEMFCs, as recently pointed out by Mustain et al.

Since AEMs are often based on hydrocarbon or aromatic backbones, the risk of enhanced susceptibility to degradation by free radicals should be considered. The possible formation of superoxide anion radical species was taken into account when discussing oxidative degradation (Scheme 1). Ex situ experiments have shown that hydroxyl and superoxide anion radicals formation, resulting from the auto-oxidation process under alkaline conditions, causes damage in the AEM polymer by backbone chain scission and functional group degradation. Furthermore, oxidative stability
of the AEMs has been estimated by monitoring the mass loss and ion-exchange capability (IEC) of samples by Fenton’s reagent. The obtained results showed a gradual decrease in the weight of the membrane, which implied the decomposition of anion-exchange groups induced by Fenton’s reagent. In addition, visible changes in membrane color and loss of mechanical properties after stability testing suggest degradation of the polymer backbone that could have been caused by an attack of free radicals (Scheme S2).

Besides electrochemical creation of reactive oxygen species (ROS) during AEMFC operation, superoxide and hydroxyl radicals can both be spontaneously created inside the AEMs in the presence of oxygen and OH⁻ ions. The radical creation mechanism is shown in Scheme 1. At the high pH of AEMs (≈9), the concentration of superoxide radicals, O₂⁻, is 2 × 10⁻⁹ times higher than hydroperoxyl, ^*OH (pKₐ = 4.7), and for a hydroxyl radical (pKₐ = 11.9) [HO^⁻/O^−] ≈ 800. Generation of ROS and other radicals during AEMFC operation is still not very well documented, although the presence of superoxide radicals was recently proposed on the basis of results obtained by in situ fluorescence spectroscopy.

In the present study we describe experiments that undoubtedly prove the formation of radicals during AEMFC operation. Four different AEMs were used in this study, (i) hydrocarbon backbone membrane with quaternary ammonium groups (Tokuyama, Japan), marked A201; (ii) radiation-grafted membrane containing covalently bonded benzyltrime-thylammonium head-groups fabricated low-density polyethylene (LDPE) (Prof. Varcoe, University of Surrey, UK); (iii) membrane composed of 2,2',4,4',6,6'-hexamethylpiperidine, and N-methylated poly(benzimidazolium)s, denoted PMBI‘ (Prof. Holdcroft, Simon Fraser University, Canada); and (iv) commercial FAA-3-PK-130 membrane, marked FAA3 (Fumatech, Germany). More information about the AEMs can be found in the Supporting Information.

AEMs were investigated in order to determine the formation of ROS in working AEMFCs and their potential role in polymer degradation. We used the electron paramagnetic resonance (EPR) spectroscopy to quantitatively study long-lived radicals and the spin trapping technique for the determination of the type of radicals. The last method is based on the scavenging of short-lived radicals by spin traps and the formation of more stable adducts, typically nitroxide radicals. In most cases, the EPR spectra of spin adducts exhibit hyperfine splitting (HFS) from ^14N and ^1H nuclei, and from these parameters it is often possible to identify the trapped radicals (for more details see the Supporting Information). As mentioned above, there are a few reports in the literature regarding the formation of free radicals in AEMFCs. However, to the best of our knowledge, the creation of stable radicals due to AEM degradation in an operating AEMFC, accompanied by the identification of the full set of free radicals (H⁺, ^*OH, and ^*OOH) and the determination of the specific place (anode/cathode) where they are formed, are reported here for the first time. The detection and identification of reactive intermediates generated during AEMFC operation provide critical information to understand and counteract the radical mechanism of AEM degradation during cell operation. This, in turn, may inspire the design and synthesis of novel anion-conducting polymers resistant to the oxidizing environment of AEMFCs.

Both the LDPE and A201-based AEMs were tested at 60 °C for 700 and 800 h, respectively, as AEMFCs. Additional information regarding the test conditions can be found in the Supporting Information. Figure 1a shows the results of the 700 h stability test of the LDPE-based AEMFC held at a constant current density of 22 mA cm⁻² and power density of 150 mW cm⁻², respectively.

![Figure 1](https://dx.doi.org/10.1021/acs.jpclett.0c02349)  
Figure 1. Voltage behavior of the (a) LDPE-based AEMFC and (b) A201-based AEMFC during a 700 and 800 h continuous operation under a constant current density of 22 mA cm⁻² and power density of 150 mW cm⁻², respectively.

As can be seen from the EPR spectra, for both AEMFC tests, the membranes show EPR signals indicating the presence of radicals. EPR spectra of the both membrane samples (from the S1 part for A201 and from the Q1–Q4 pieces of LDPE-base membrane) are presented in Figure 2. In the case of LDPE-
based membrane the EPR spectrum from pieces of the external (nonactive) part of the same membrane was used as the reference. In this way we are assured that the reference membrane piece was exposed to the same temperature, humidity, and storage time after testing as was the active sample, but without electrochemical activation and direct contact with oxygen.

EPR spectra of A201 and LDPE membranes operated in AEMFCs are given in Figure 2a,b, respectively. The EPR signals were observed even after storing the samples for several weeks at ambient temperature. The EPR signals from the A201 sample were simulated as a superposition of three signals with a slightly different $g$ value $g_{A201-I} = 2.0046$, $g_{A201-II} = 2.0035$, and $g_{A201-III} = 2.0018$ (Figure 2a) whereas the one from LDPE consists of two lines with magnetic parameters $g_{LDPE-I} = 2.0037$ and $g_{LDPE-II} = 2.0030$ (Figure 2b). According to the literature data, the signals might be attributed to oxygen centered radicals, since the $g$ values are higher than that of free electron ($g_e = 2.0023$) and carbon centered radicals. We suggest that the stable radicals detected in both AEMs are the results of the attack on the backbones of the membranes by short living oxygen radicals created during AEMFC operation. This hypothesis is supported by the fact that the intensity of the signal depends strongly on the position in the membrane in relation to the inlet and outlet of feeding gases into the cell (see Scheme 2). In both cases, A201 and LDPE AEMs, the highest EPR signal intensity, and thus concentration of radicals, was observed from membrane parts located closest to the inlet of oxygen gas ($S_1$ and $Q_1$). Additionally, the intensity of the EPR signal from radicals created in the active part of the LDPE-based membrane was clearly higher in comparison with the reference sample (100 au versus 6 au, respectively), suggesting a much faster membrane degradation under AEMFC operating conditions. Furthermore, literature data describing degradation of the hydrocarbon polymers and model compounds consider the significant role of the radical attack.

To further investigate the formation of radical species during AEMFC operation, in situ EPR measurements were performed using a micro fuel cell inserted into the spectrometer cavity. The spin trapping technique was used to detect and identify the short living species. During in situ testing, DMPO spin trap was placed on the investigated electrode (anode or cathode) of a micro-AEMFC made with a catalyst layer. Registered spectra were afterward simulated using SimEPR 32 software in order to determine EPR parameters for each component. The error of the $g$ factors determination was estimated as $\pm 0.0002$, whereas in the case of hyperfine splitting constants as $\pm 0.1$ G.

For all investigated in situ AEMs, namely, LDPE, HMT-PMBI, and FAA-3, the EPR signals registered on the anode side (Figure 3 and Figure S1), consisted of only one component, which can be undoubtedly associated with the presence of DMPO-H adducts, based on the magnetic

**Figure 2.** Experimental (solid black line) and simulated (dashed red line) EPR spectra of the radicals in A201 (a) and LDPE (b) AEMs after long-term AEMFC tests. EPR spectrum of the reference LDPE membrane is also given (solid blue line), the signal intensities were normalized to the samples weight.

**Figure 3.** EPR experimental (black line) and simulated (red dashed line) spectra of DMPO radicals adducts recorded on the anode side of micro-AEMFC using LDPE-based membrane.
parameters given in Table 1 and literature data. The detected \( \text{H}^- \) radicals can be created in the splitting reaction of molecular hydrogen on the platinum catalyst surface. The EPR signal registered on the cathode side of the micro-AEMFC cell using a LDPE membrane (Figure 4a) consists of three components. The first component with \( g = 2.0062, a_N = 13.0 \text{ G}, a_{H\beta} = 10.2 \text{ G}, \text{ and } a_{H\gamma} = 1.4 \text{ G} \) and the second one characterized by \( g = 2.0060, a_N = 14.0 \text{ G}, a_{H\beta} = 11.7 \text{ G}, \text{ and } a_{H\gamma} = 0.9 \text{ G} \) are assigned to DMPO-OOH adducts present in two environments that differ in local polarity. The DMPO spin trap can react with \( \cdot \text{OOH} \) and \( \cdot \text{O}_2^- \) radicals leading to the formation of DMPO-OOH radicals in both cases. The only difference is that, according to this kinetic model, the reaction with hydroperoxide radicals dominates below pH 7.7, while the second one characterized by \( g = 2.0058, a_N = 17.4 \text{ G} \) is due to radical products of the spin trap decomposition (Figure 4b). Also in the case of the HMT-PMBI membrane, on the cathode side (Figure S2b), DMPO-OOH adducts were detected (\( g = 2.0061, a_N = 13.8 \text{ G}, a_{H\beta} = 11.8 \text{ G}, \text{ and } a_{H\gamma} = 0.7 \text{ G} \)). The magnetic parameters determined by \textit{in situ} EPR spin trapping technique for all DMPO adducts are summarized in Table 1.

In summary, the results presented in this study clearly prove the formation and presence of radicals during and after AEMFC operation. The EPR investigations indicate that, in addition to the known chemical degradation mechanisms of the cationic ammonium groups of the membrane, oxidative degradation including radical reactions has to be taken into account when the stability of an anion conductive polymer for AEMFCs is investigated. Formation of stable radicals in AEMs was proven for the first time in this study. All short living radicals formed during the AEMFC operation were fully identified. The presence of radicals in the AEM after AEMFC testing indicates that reactive oxygen species may play a very important role in the degradation mechanism of the anion conducting polymers. Results from this study shed light on the understanding of radical formation and presence in the membranes during AEMFC tests, which in turn may help to solve the challenge of stability in this technology.

### Table 1. Spectral Parameters for All Recorded Spectra

| AEM/electrode       | radical     | hyperfine splittings | \( \text{g} \)  |
|---------------------|-------------|----------------------|------------------|
| FAA-3/anode         | DMPO-H      | \( a_N = 15.9 \text{ G} \), \( a_{H\beta} = 21.5 (2\text{H}) \text{ G} \), \( a_{H\gamma} = 0.9 \text{ G} \) | 2.0053 |
| FAA-3/cathode       | DMPO-OOH    | \( a_N = 13.9 \text{ G} \), \( a_{H\beta} = 11.7 \text{ G} \), \( a_{H\gamma} = 1.4 \text{ G} \) | 2.0057 |
| LDPE/anode          | DMPO-H      | \( a_N = 16.0 \text{ G} \), \( a_{H\beta} = 21.6 (2\text{H}) \text{ G} \), \( a_{H\gamma} = 0.9 \text{ G} \) | 2.0052 |
| LDPE/cathode        | DMPO-OOH    | \( a_N = 13.0 \text{ G} \), \( a_{H\beta} = 13.0 \text{ G} \), \( a_{H\gamma} = 1.4 \text{ G} \) | 2.0058 |
| LDPE/anode          | DMPO-H      | \( a_N = 15.6 \text{ G} \), \( a_{H\beta} = 21.0 (2\text{H}) \text{ G} \), \( a_{H\gamma} = 0.9 \text{ G} \) | 2.0056 |
| LDPE/cathode        | DMPO-OOH    | \( a_N = 13.0 \text{ G} \), \( a_{H\beta} = 10.2 \text{ G} \), \( a_{H\gamma} = 1.4 \text{ G} \) | 2.0062 |
| HMT-PMBI/anode      | DMPO-H      | \( a_N = 14.0 \text{ G} \), \( a_{H\beta} = 11.7 \text{ G} \), \( a_{H\gamma} = 0.9 \text{ G} \) | 2.0059 |
| HMT-PMBI/cathode    | DMPO-OOH    | \( a_N = 13.8 \text{ G} \), \( a_{H\beta} = 11.8 \text{ G} \), \( a_{H\gamma} = 0.7 \text{ G} \) | 2.0061 |

![Figure 4. EPR spectra of DMPO radical adducts recorded during operation of micro-AEMFC using LDPE (a) and FAA-3 (b) membranes. Experimental spectra are marked black, simulated spectra are red, and components of simulated spectra are blue, green, and purple.](https://dx.doi.org/10.1021/acs.jpclett.0c02349)
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**Notes**

The authors declare no competing financial interest.

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