**In-situ** spin trap electron paramagnetic resonance study of fuel cell processes

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A novel method allows the monitoring of radical formation and membrane degradation in-situ in a working fuel cell which is placed in the microwave resonator of an electron paramagnetic resonance (EPR) spectrometer. By introduction of a spin trap molecule at the cathode the formation of immobilized organic radicals on the membrane surface is observed for F-free membranes, revealing the onset of oxidative degradation. For Nafion® there is much less evidence of degradation, and the hydroxyl radical is detected instead. At the anode, free radical intermediates of the fuel oxidation process are observed. No traces of membrane degradation are detected on this side of the fuel cell.

It is generally believed that fuel cells will play an important role in energy supply already in the near future.1–3 High efficiency, low emission, fuel diversification, and silence are important advantages.4–6 One of the most promising types is the Polymer Electrolyte Membrane Fuel Cell (PEMFC), but several shortcomings have to be overcome prior to its large-scale introduction to the market. Most crucial is its lifetime, for which more than 40,000 h of continuous and stable performance are required. Poisoning of the platinum-based anode catalysts by partial oxygen crossover through the membrane degradation can take place also at the anode. A PEM based on an inert aliphatic perfluorocarbon sulfonic acid known as Nafion® has an inherent advantage over alternative membranes based on aromatic hydrocarbons. The perfluorinated membrane should show no significant degradation on the experimental time scale,12 but serious disadvantages include its high price and high methanol permeability in cells using methanol as a fuel, leading to severe reduction of the performance.13 The needs for new membrane materials are thus extremely high.

Conventional in-situ analysis of fuel cells is limited mostly to static and dynamic electrochemical methods, in particular current–voltage characteristics and impedance spectroscopy or cyclovoltammetry. They cannot easily differentiate between cathode and anode. Aiming at complementary and more selective information we developed a cell capable of operating in the resonator of an X-band EPR-spectrometer.14 Here it is shown that it permits the direct observation and monitoring of radical formation. The work aims at an understanding of the pathways of oxidative degradation of membranes, and it wants to provide guidance in the choice of favorable fuel cell operating conditions and in the preparation of alternative membranes with improved durability.

The in-situ fuel cell consists of two Teflon® half-cylinders. Gas feeding channels inside each half-cylinder admit oxygen and hydrogen. The active part includes a Pt mesh as a spacer and hydrogen and oxygen. The membrane, a key component, consists of an organic polymer with pendant sulfonic acid groups which are necessary for H⁺ transport from the anode to the cathode. Only extremely stable membranes can withstand the aggressive chemical and physical environment in an operating fuel cell.7 Within a given set of operating conditions, intrinsic chemical and mechanical properties of the membrane as well as its water content impact its durability dramatically.

Hydroxyl and superoxide radicals are regular intermediates of the cathode reaction. This is unproblematic as long as they remain attached to the catalyst surface. Hydrogen peroxide is formed at low index Pt surfaces at the cathode. It is set free in trace amounts and found in product water.11 In the presence of noble metals and at elevated temperatures H₂O₂ decays into hydroxyl radicals which attack the membrane.10 Because of partial oxygen crossover through the membrane degradation can take place also at the anode. A PEM based on an inert aliphatic perfluorocarbon sulfonic acid known as Nafion® has an inherent advantage over alternative membranes based on aromatic hydrocarbons. The perfluorinated membrane should show no significant degradation on the experimental time scale,12 but serious disadvantages include its high price and high methanol permeability in cells using methanol as a fuel, leading to severe reduction of the performance.13 The needs for new membrane materials are thus extremely high.

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The in-situ fuel cell consists of two Teflon® half-cylinders. Gas feeding channels inside each half-cylinder admit oxygen and hydrogen. The active part includes a Pt mesh as a spacer that allows gas distribution and at the same time provides electrical contact, and a Catalyst Coated Membrane (CCM, that is a membrane with Pt electrodes deposited on both sides). For the CCM production the dry Pt powder (grain size ca. 30 nm) is blown onto the membrane. This results in a uniformly distributed catalyst which is fixed to the membrane in a rolling process by passing it through a calender.15 The Pt...
loading corresponds to 0.77 mg cm\(^{-2}\). Nafion\(^{\circledR}\) 115 and a F-free polyaryl-blend covalently cross-linked membrane (composition: 67.3 wt.% poly(etherketone), 32.7 wt.% polyether-sulfone, and 1,4-diiodobutane crosslinker) were employed. The novel membrane shows promising chemical and thermal stability, good proton conductivity, and good performance in a direct methanol fuel cell.\(^{15}\)

The concentration of free radicals produced in a fuel cell is extremely low and their lifetime is relatively short, so that it is not possible with conventional methods to observe them directly. We therefore employed the spin-trapping technique, using the spin trap molecules alpha-(4-pyridyl-1-oxide)-N-tert-butylnitrone (POBN) and 5,5-dimethyl-1-pyrroline 1-oxide (DMPO) obtained from Aldrich. It allows the trapping of short-lived radicals under the formation of relatively stable nitroxide radicals (the spin adducts) which are detectable by EPR.\(^{17}\) The spin trap solution is applied separately at the anode or the cathode side, permitting selective investigation of radical formation and of degradation reactions.

We first discuss radical formation at the anode side. 10 \(\mu\)L of 1 M aqueous solution of POBN is deposited on the electrode. After five minutes of operation the POBN-'H adduct is detected (Fig. 1a). The spectrum is characterized by a \(g\)-factor of 2.0056 that is typical for POBN radical adducts, and it consists of a triplet of triplets due to 1:1:1 and 1:2:1 splittings by one \(^{14}\)N \((\Delta g_{14} = 15.10 \text{ G})\) and by two equivalent \(^{1}\)H \((\Delta g_{1} = 9.82 \text{ G})\) nuclei, respectively. The peak-to-peak line width \((\Delta H_{pp})\) amounts to 0.83 G. The result does not depend on the nature of the membrane.

The mechanism of formal H atom addition to the spin trap molecule is studied further in the following set of experiments: the fuel cell is fed with H\(_2\) or D\(_2\), and the POBN solution is applied. Both of these additions result in the spectrum shown in Fig. 1a. No influence of D\(_2\) was observed. Then, the two experiments are repeated, but now using a heavy water solution of the spin trap. As a result the formal D adduct to POBN was observed, as revealed by the additional splitting (Fig. 1b). This is evidence of a mechanism involving reduction of POBN at the electrode surface followed by protonation by solvent molecules, H\(_2\)O or D\(_2\)O:

\[
\text{POBN} + \text{H}_2\text{O} \rightarrow \text{POBN-H}\]

\[
\text{POBN} + \text{D}_2\text{O} \rightarrow \text{POBN-D}\]

\[
\text{POBN-H} \rightarrow \text{POBN} + \text{H}^+ + \text{e}^-\]

\[
\text{POBN-D} \rightarrow \text{POBN} + \text{D}^+ + \text{e}^-\]

\[
\text{POBN-H} + \text{D}_2\text{O} \rightarrow \text{POBN-D} + \text{H}_2\text{O}\]

\[
\text{POBN-D} + \text{H}_2\text{O} \rightarrow \text{POBN-H} + \text{D}_2\text{O}\]

Alternatively, a fast isotope exchange could take place on the catalyst surface before the atom is trapped by POBN.

For comparison, Fig. 2a shows a spectrum obtained after UV photolysis of hydrogen peroxide in an ethanol-water solution in the presence of POBN. H\(_2\)O\(_2\) decays into two 'OH radicals. These react by hydrogen abstraction with CH\(_3\)CH\(_2\)OH molecules to form CH\(_3\)CHOH and CH\(_3\)CH\(_2\)OH radicals (thereafter denoted 'R'). These short-lived radicals are scavenged by POBN, resulting in a stable POBN-'R adduct radical.\(^{18,19}\) Its spectrum consists of the characteristic triplet of doublets shown in Fig. 2a and has the following parameters: \(\Delta g_{14} = 15.45 \text{ G}, \Delta g_{1} = 2.70 \text{ G}, \Delta H_{pp} = 1.00 \text{ G}\). While the H adduct (Fig. 1a) is well distinguished from that of a trapped organic radical the splittings due to nuclei further remote than the one which makes the bond to the spin trap are normally too small to be resolved so that a distinction between different organic radicals is not normally possible.

Ethanol is one of the potential fuels under investigation for direct conversion in fuel cells. Depositing an ethanol–water solution of POBN on the anode equipped with a Nafion\(^{\circledR}\) based CCM, and operating the cell for 5 min under closed circuit conditions results in the spectrum shown in Fig. 2b. It is a superposition of the H adduct spectrum shown in Fig. 1a and, interestingly, the R-adduct from Fig. 2a. In the absence of 'OH the latter must arise from partial oxidation of ethanol which can also serve as a fuel in a PEMFC. At the cathode, in contrast, 'OH radicals can be formed and attack ethanol molecules, leading to the same spin adduct as in Fig. 2a (Fig. 2c).

In order to study membrane degradation 10 \(\mu\)L of 1 M aqueous solution of POBN was deposited on the cathode side of the fuel cell equipped with Nafion\(^{\circledR}\) or a F-free membrane based CCM. The current circuit was closed for 5 min before the EPR spectra were recorded under open circuit conditions (Fig. 3). The experimental conditions were the same as for the ethanol studies at the anode and cathode sides of the fuel cell. The experiment using a Nafion\(^{\circledR}\) membrane has a very weak signal (Fig. 3a), while a F-free membrane exhibits a strong six-line spectrum corresponding to nitroxide radicals immobilised at the membrane surface (Fig. 3b, parameters: \(\Delta g_{14} = 15.10 \text{ G}, \Delta g_{1} = 2.68 \text{ G}, \Delta H_{pp} = 1.51 \text{ G}\) for the first four lines and 1.91 G for the doublet at high field). During oxygen reduction at the cathode 'OH radicals as intermediates of the process are formed on the Pt surface.\(^{20}\) In the presence of water a small fraction of the radicals may leave the electrocatalyst and attack the membrane.\(^{21}\)

For the purpose of distinguishing 'OH radicals formed during oxygen reduction an aqueous DMPO solution was
applied at the cathode.\textsuperscript{22} In this experiment the CCM was based on a Nafion\textsuperscript{16} membrane. Fig. 4 depicts the characteristic spectrum corresponding to the DMPO–\textsuperscript{•}OH adduct\textsuperscript{23,24} recorded after 5 min of closed circuit operation. DMPO–\textsuperscript{•}OH can also originate from the spontaneous decay of a DMPO–superoxide adduct (DMPO–\textsuperscript{•}OOH).\textsuperscript{25}

The dominating reaction of the \textsuperscript{•}OH (and \textsuperscript{•}OOH) radical intermediates is addition to the aromatic rings. After several consecutive reactions this can lead to the loss of -SO\textsubscript{3}H groups.\textsuperscript{10,26} Such losses are critical for the membrane performance since they lead to the reduction of proton conductivity.\textsuperscript{8,26}

\textsuperscript{•}OH radical attack leads to organic radicals which are immobilized on the membrane surface. POBN reacts with these radicals to form stable adducts which are detectable by means of EPR and which we observe in Fig. 3b:

![Scheme 2](image)

The key point is that immobilized radicals at the membrane surface cannot reorient isotropically, and hyperfine anisotropy is not fully averaged out. They thus reveal a spectrum with much broader lines than in water solution where they can tumble freely and average isotropically (compare Fig. 3 with Fig. 2a and c). This additional line width is not attributed to spin exchange with oxygen, as Fig. 2c shows much narrower lines under similar conditions. The lines in Fig. 3b are not fully resolved, especially for the doublet at high field. The broad lines provide the first direct evidence that a membrane is degraded via radical reactions in a working fuel cell.

The signal in Fig. 3a may originate from almost negligible degradation of the Nafion\textsuperscript{16} membrane and/or from traces of POBN partial oxidation products. It is not surprising that this perfluorinated membrane is more inert towards degradation despite the fact that \textsuperscript{•}OH radicals are present and can be trapped (Fig. 4).

In summary, we have developed a method for the direct investigation of radical processes in a running fuel cell. This first work reports the observation of intermediates of the anode reaction when either hydrogen or ethanol are used as a fuel, and it provides evidence for radical centres produced at the cathode side of the polymer membrane as a likely intermediate of oxidative degradation via free radical processes. It opens numerous possibilities for more quantitative studies of membrane degradation, mechanisms of oxygen reduction, and fuel oxidation. Systematic studies as a function of current and voltage, temperature, gas pressure, and membrane humidity are expected to reveal what the critical operating parameters are which lead to membrane degradation in a fuel cell. The spin trap technique is not limited to POBN and DMPO. Preliminary spin trap studies with 3,5-dibromo-4-nitrosobenzene-sulfonic acid (DBNBS)\textsuperscript{27} support the present observations with POBN.

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References