Possible repair mechanism for hydrocarbon-based ionomers following damage by radical attack

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Supporting Information

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1. General

Cerium(IV) sulfate anhydrous 97% (Alfa Aesar), Cerium(III) sulfate anhydrous 99.99% (Sigma Aldrich), hydrogen peroxide 30% w/v (Fischer Scientific), sulfuric acid 95% (Fischer Scientific), potassium persulfate were used as received. Potassium phosphate buffer (KPi) was prepared from potassium phosphate dibasic and potassium phosphate monobasic. Ultra-pure water was provided by a Milli-Q or Evoqua Ultra Clear UV Plus water purification system.

_Pulse radiolysis study:_

Experiments were carried out with the 2 MeV Febetron 705 accelerator of ETH. The equipment delivered <50 ns pulses of 2–100 Gy, with 1 Gy = 1 J/kg. Absolute doses were determined by KSCN dosimetry, based on $G = 6.13$ and $\varepsilon_{472} = 7.580 \text{ M}^{-1}\text{cm}^{-1}$, where the radical chemical yield $G$ refers to number of species created per 100 eV absorbed dose and $G = 1$ is equal to 0.1036 µmol generated species per 1 J/kg = 1 Gy absorbed energy.2 Samples were gas saturated in Schlenk-tubes sealed with rubber septa which were repeatedly evacuated to 10 mbar and refilled (a minimum of 3 repeats) with the desired gas. The solutions then were transferred to a gas-tight syringe (10 ml, Hamilton, SampleLock, Bonaduz, Switzerland), which was connected to the 6 cm quartz irradiation-cell (Hellma, Mülhausen, Germany) via a syringe pump. Acidic pH was established with H$_2$SO$_4$ (95-97%). Experiments were carried out at 24°C, 25°C, 37°C, 47°C, 62°C and 70°C, respectively. Temperature in the cell was controlled by a Lauda e100 thermostat.

_UV/Vis measurements:_

UV/vis measurements were performed using a Cary 4000 UV/Vis spectrophotometer (Varian, Palo Alto, USA) in dual beam mode and was used to measure the absorption spectra of Ce(III) sulfate and Ce(IV) sulfate species in 0.1 M sulfuric acid. The extinction coefficients were determined using Beer-Lambert’s law.
2. Pulse radiolysis supporting information

Table S1. Initial radical reactions during pulse radiolysis.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>$k$ (M$^{-1}$s$^{-1}$)</th>
<th>Conc (mM)</th>
<th>$k'$ (s$^{-1}$)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^*$</td>
<td>S$_2$O$_8^{2-}$ + HO$^<em>$ → S$_2$O$_8^{</em>}$ + HO$^-$</td>
<td>1.2·10$^7$</td>
<td>100</td>
<td>1.2·10$^6$</td>
<td>A-9$^3$</td>
</tr>
<tr>
<td></td>
<td>S$_2$O$_8^{2-}$ + HO$^<em>$ → S$_2$O$_8^{</em>}$ + HO$^-$</td>
<td>1.2·10$^7$</td>
<td>10</td>
<td>1.2·10$^5$</td>
<td>A-9$^3$</td>
</tr>
<tr>
<td>P + HO$^*$ → *P-OH</td>
<td>2.8·10$^7$</td>
<td>1</td>
<td>2.8·10$^7$</td>
<td>1$^4$</td>
<td></td>
</tr>
<tr>
<td>e$_{\text{(aq)}}^-$</td>
<td>e$_{\text{aq}}^-$ + H$^+$ → H$^*$</td>
<td>2·10$^{10}$</td>
<td>1</td>
<td>2·10$^7$</td>
<td>A-3$^5$</td>
</tr>
<tr>
<td>e$_{\text{aq}}^-$</td>
<td>e$_{\text{aq}}^-$ + H$^+$ → H$^*$</td>
<td>2·10$^{10}$</td>
<td>10</td>
<td>2·10$^8$</td>
<td>A-3$^5$</td>
</tr>
<tr>
<td>e$_{\text{aq}}^-$</td>
<td>e$_{\text{aq}}^-$ + H$^+$ → H$^*$</td>
<td>2·10$^{10}$</td>
<td>100</td>
<td>2·10$^9$</td>
<td>A-3$^5$</td>
</tr>
<tr>
<td>S$_2$O$<em>8^{2-}$ + e$</em>{\text{aq}}^-$ → SO$_4^{*}$ + SO$_4^{2-}$</td>
<td>1.2·10$^{10}$</td>
<td>10</td>
<td>1.2·10$^8$</td>
<td>A-2$^5$</td>
<td></td>
</tr>
<tr>
<td>S$_2$O$<em>8^{2-}$ + e$</em>{\text{aq}}^-$ → SO$_4^{*}$ + SO$_4^{2-}$</td>
<td>1.2·10$^{10}$</td>
<td>100</td>
<td>1.2·10$^9$</td>
<td>A-2$^5$</td>
<td></td>
</tr>
<tr>
<td>N$_2$O + H$<em>2$O + e$</em>{\text{(aq)}}^-$ → N$_2$ + HO$^*$ + HO$^-$</td>
<td>9·10$^9$</td>
<td>24.8</td>
<td>2.2·10$^8$</td>
<td>A-4$^5$</td>
<td></td>
</tr>
<tr>
<td>H$^*$</td>
<td>S$_2$O$_8^{2-}$ + H$^<em>$ → SO$_4^{</em>}$ + SO$_4^{2-}$ + H$^+$</td>
<td>1.4·10$^7$</td>
<td>10</td>
<td>1.4·10$^5$</td>
<td>A-5$^6$</td>
</tr>
<tr>
<td>P + H$^*$ → *P-H</td>
<td>1.95·10$^{10}$</td>
<td>1</td>
<td>1.95·10$^7$</td>
<td>A-6$^7$</td>
<td></td>
</tr>
<tr>
<td>SO$_4^{*}$</td>
<td>P + SO$_4^{<em>}$ → P$^{</em>+}$ + SO$_4^{2-}$</td>
<td>9·10$^8$</td>
<td>1</td>
<td>9·10$^5$</td>
<td>7$^8$</td>
</tr>
</tbody>
</table>

We optimized our reaction conditions to make sure our main products are *P-OH, reaction (1), and P$^*$, reaction (7).
Figure S1. Dose-normalized kinetic traces for the reaction between PAMSS-14'600 cation radical and Ce(III), \( N=3-5 \), taken at \( \lambda = 560 \) nm, in irradiated (dose of ca. 21–37 Gy) argon saturated 10 mM K₂S₂O₈ solutions that contained 1 mM H₂SO₄, 0.1 mM PAMSS-14600 and 0.2mM Ce(III) (blue), 0.3 mM PAMSS-14600 and 0.6 mM Ce(III) (red), 1 mM PAMSS-14600 and 2 mM Ce(III) (black) recorded at 24°C (Top left), 47°C (Top right) and 70°C (Bottom).
**Figure S2.** Dose-normalized kinetic traces for the self-decay of PAMSS-14’600 cation radical, \(N=3\), taken at \(\lambda = 560\) nm, in irradiated (dose of ca. 10–29 Gy) argon saturated 10 mM K\(_2\)S\(_2\)O\(_8\) solutions that contained 1 mM H\(_2\)SO\(_4\), 0.1 mM PAMSS-14600 at 24°C (blue), 47°C (red) or 70°C (black). Traces were normalized to the maximum absorbance of each trace.

**Figure S3.** Pseudo-first-order rate constants for the reaction of 0.1, 0.3, 1 mM PAMSS-14’600 cation radical with 0.2, 0.6 and 2 mM Ce(III) as a function of concentration at 24 °C (blue), 47 °C (red) and at 70 °C (black) in irradiated (dose of ca. 20–40 Gy) argon saturated 10 mM K\(_2\)S\(_2\)O\(_8\) solutions that contained 1 mM H\(_2\)SO\(_4\), recorded at \(\lambda = 560\) nm.
For the purpose of obtaining the rate constants of self-decay of the HO-adduct at different temperatures kinetic traces detected at 320 nm were recorded for $T = 25^\circ C$, $37^\circ C$ and $62^\circ C$ at pH=7 (Figure S4). Neutral pH was chosen for shifting the protolysis equilibrium towards the HO-adduct.

![Figure S4](image)

**Figure S4.** Dose-normalized kinetic traces for the self-decay of PAMSS-14’600 HO-adduct, $N=3$, taken at $\lambda = 320$ nm, in irradiated (dose of ca. 9–16 Gy) argon or N2O saturated solutions that contained 0.1 mM KPi buffer and 0.1 mM PAMSS-14600 at 25°C (blue), 37°C (red) or 62°C (black). Traces were normalized to the maximum absorbance of each trace.
Figure S5. Left panel: Arrhenius plot of the decay of PAMSS* in the absence (top) and in the presence of Ce(III) (bottom), estimated experimentally. Right panel: Arrhenius plot of the decay of HO-adduct in the absence of O₂, estimated experimentally.
3. Calibration of [Ce(III)] and [Ce(IV)] determinations

Figure S6. Absorption spectra of Ce$_2$(SO$_4$)$_3$ in 0.1 M H$_2$SO$_4$

Figure S7. Absorption spectra of Ce(SO$_4$)$_2$ in 0.1 M H$_2$SO$_4$
**Figure S8.** Calibration curve: absorption maximum of Ce$_2$(SO$_4$)$_3$ as a function of concentration. 5 mM outlier excluded (marked red) from the linear fit. Extinction coefficient determined with Beer-Lambert’s law, $\varepsilon = 0.66 \pm 0.01$ mM$^{-1}$ cm$^{-1}$

**Figure S9.** Calibration curve: absorption maximum of Ce(SO$_4$)$_2$ as a function of concentration. 0.5 mM outlier excluded (marked red) from the linear fit. Extinction coefficient determined with Beer-Lambert’s law, $\varepsilon = 4.89 \pm 0.04$ mM$^{-1}$ cm$^{-1}$
4. Stopped-flow measurements

**Figure S10.** Kinetics trace of 0.3 mM H$_2$O$_2$ reacting with 0.03 mM Ce(IV) at 50 °C (black squares) with an exponential fit (red line). Initially the reaction of hydrogen peroxide with cerium(IV) can be seen by the first-order decay of the absorption signal followed by a slow increase. This secondary process is not studied in detail and is too slow to be reaction (6).
**Figure S11.** Observed first-order rate constant plotted as a function of Ce(IV) concentration at different temperatures (black = 10°C, blue = 25°C, red = 50°C, green = 74°C) where Ce(IV) was in a 10-fold excess to H₂O₂ (see Appendix B for the exact composition). The second-order rate constant is derived from the slope of the linear fit.

**Table S2** Rate constants $k_6$ derived from the control measurements (H₂O₂ in excess).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>2nd order rate constant $k_6$ (10⁵ M⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.3</td>
</tr>
<tr>
<td>25</td>
<td>2.5</td>
</tr>
<tr>
<td>50</td>
<td>6.7</td>
</tr>
<tr>
<td>75</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Figure S12. Arrhenius plot of reaction (6), where the reaction rate was measured in Ce(IV) excess (black circles) and H$_2$O$_2$ excess (red squares). The high temperature point for H$_2$O$_2$ excess has been excluded in the fit due to noticeable thermal decomposition during the measurement (open square).
5. Rate of polymer attack $r_{\text{HO}}$

We need to identify a reasonable value for the rate of radical formation $r_{\text{HO}}$ to be used in the model. We consider this rate to be equal to the rate of attack of aromatic units in the polymer because other reactions of HO$^\cdot$ are expected to be much slower.\textsuperscript{9} Although the relative effectiveness of damage mitigation is independent of $r_{\text{HO}}$ (cf. main text, equations 9 and 10), the value is important to estimate the concentration ratio of Ce(IV) to Ce(III), since only Ce(III) is the active repair agent. We can obtain a rough estimate of the rate of HO$^\cdot$ formation from fluoride emission rate (FER) data from perfluoralkylsulfonic acid (PFSA) membranes. Under accelerated degradation (OCV hold) test conditions at temperatures in the range between 60 to 90°C, a fluoride emission rate in the range of $10^{-7}$ to $10^{-6}$ mol·cm$^{-2}$·h$^{-1}$ is measured.\textsuperscript{10} Considering two hydrogen fluoride (HF) molecules are emitted per attack of HO$^\cdot$, and using a membrane thickness of 50 µm, we obtain a rate of attack on the ionomer by HO$^\cdot$ in the range of $5\times10^{-6}$ to $5\times10^{-5}$ M·s$^{-1}$. However, in PFSA ionomer not all of the HO$^\cdot$ formed reacts with the polymer. Instead, a sizeable fraction reacts with H$_2$ (at least near the anode side).\textsuperscript{10} If we estimate the probability of an attack of HO$^\cdot$ on the PFSA ionomer of 50%, the rate of formation of HO$^\cdot$ would be in the range of $10^{-5}$ to $10^{-4}$ M·s$^{-1}$. Radical formation in fuel cell membrane electrode assemblies (MEAs) is, to a large extent, governed by crossover of H$_2$ and O$_2$ through the membrane. In hydrocarbon based membranes, the gas permeability can be lower by a factor of 20 when compared to PFSA membranes.\textsuperscript{11, 12} Therefore, we estimate the rate of HO$^\cdot$ formation in a hydrocarbon-based MEA to be in the range of $5\times10^{-7}$ to $5\times10^{-6}$ M·s$^{-1}$. In our simulation, we use a value of $r_{\text{HO}} = 10^{-6}$ M·s$^{-1}$, which represents a reasonable value for an OCV hold test. If we assume an attack of 10% of aromatic units to be fatal, this rate leads to a membrane lifetime of $\tau = 0.1 \cdot [P] / r_{\text{HO}} \cong 280$ h. Sethuraman et al. measured a lifetime of a hydrocarbon based membrane in a fuel cell at 100°C and open circuit hold conditions of around 350 h.\textsuperscript{11}
6. Determination of model parameters

The model parameters \([P], [P-SO_3^-] = [H^+]\) and \([H_2O]\) are obtained as follows.

A representative ion exchange capacity (IEC) of sulfonated polyarylene type ionomers is 2 mmol/g, see for example reference.\(^{13}\) In most cases, this leads to decent conductivities in the swollen state, but not to excessive water uptake and swelling. The concentration of sulfonate groups, \(P-SO_3^-\), and protons, \(H^+\), is the same, because they are derived from the dissociation of sulfonic acid \(P-SO_3H\). We assume a density of the polymer in the dry state of \(\rho_{pol} = 1.2\ \text{g/cm}^3\) and a mass based water uptake of \(s = m_w / m_{pol} = 40\%\). We can then estimate, under the assumption of a zero excess volume of mixing, the water volume fraction \(\Phi_w\):\(^{14}\)

\[
\Phi_w = \frac{V_w}{V_w + V_{pol}} = \frac{s}{s + \frac{\rho_w}{\rho_{pol}}} \quad (S1)
\]

and obtain 32\%, where we have used \(\rho_w = 1.0\ \text{g/cm}^3\). The concentration of water in the membrane is then [\(H_2O\)] = 0.32 \cdot 55 \text{ mol/L} \approx 20 \text{ M}. Using these data, we obtain for the volumetric IEC of the membrane in the water swollen state a value of \(\sim 1.5 \text{ mmol/cm}^3\). This corresponds to \([P-SO_3^-]\) and \([H^+]\).

For the estimation of the concentration of aromatic units \([P]\) we assume the following composition of our generic polyaromatic ionomer:

\[
\text{SO}_3\text{H}
\]

\text{Scheme S1}

For an IEC of 2 mmol/g, which corresponds to an equivalent weight \(\text{EW}\) of 500 g/mol, we calculate \(n = 4.5\).

Next, we calculate the molar volume \(\nu_{tot}\) of polymer with 1 mol of sulfonic acid groups and water:

\[
\nu_{tot} = \nu_{pol} + \nu_w = \left(\frac{1}{\rho_{pol}} + \frac{s}{\rho_w}\right) \cdot EW \quad (S2)
\]

Inserting the values from above we obtain \(\nu_{tot} = 0.62\ \text{L/mol}\). Since we have \(4.5 + 1\) aromatic rings in the repeating unit, the concentration of aromatic units amounts to \([P] \approx 10\ \text{M}\).
REFERENCES