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 $\epsilon_{472} = 7.580 \, \text{M}^{-1}\text{cm}^{-1}$, 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. 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 $\text{H}_2\text{SO}_4$ (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.

| Species  | Reaction                              | $k$ (M$^{-1}$s$^{-1}$) | Conc (mM) | $k'$ (s$^{-1}$) | Reaction |
|----------|---------------------------------------|------------------------|-----------|-----------------|----------|
| OH$^\bullet$ | $\text{S}_2\text{O}_8^{2-} + \text{HO}^\bullet \rightarrow \text{S}_2\text{O}_8^{\bullet} + \text{HO}^-$ | $1.2 \cdot 10^7$ | 100       | $1.2 \cdot 10^6$ | A-9$^3$ |
|          | $\text{S}_2\text{O}_8^{2-} + \text{HO}^\bullet \rightarrow \text{S}_2\text{O}_8^{\bullet} + \text{HO}^-$ | $1.2 \cdot 10^7$ | 10        | $1.2 \cdot 10^5$ | A-9$^3$ |
|          | $\text{P} + \text{HO}^\bullet \rightarrow \text{P-OH}$ | $2.8 \cdot 10^{10}$ | 1         | $2.8 \cdot 10^7$ | 1$^4$    |
| $e_{(\text{aq})}^-$ | $e_{(\text{aq})}^- + \text{H}^+ \rightarrow \text{H}^\bullet$ | $2 \cdot 10^{10}$ | 1         | $2 \cdot 10^7$ | A-3$^5$ |
|          | $e_{(\text{aq})}^- + \text{H}^+ \rightarrow \text{H}^\bullet$ | $2 \cdot 10^{10}$ | 10        | $2 \cdot 10^8$ | A-3$^5$ |
|          | $e_{(\text{aq})}^- + \text{H}^+ \rightarrow \text{H}^\bullet$ | $2 \cdot 10^{10}$ | 100       | $2 \cdot 10^9$ | A-3$^5$ |
|          | $\text{S}_2\text{O}_8^{2-} + e_{(\text{aq})}^- \rightarrow \text{SO}_4^{\bullet^-} + \text{SO}_4^{2-}$ | $1.2 \cdot 10^{10}$ | 10        | $1.2 \cdot 10^8$ | A-2$^5$ |
|          | $\text{S}_2\text{O}_8^{2-} + e_{(\text{aq})}^- \rightarrow \text{SO}_4^{\bullet^-} + \text{SO}_4^{2-}$ | $1.2 \cdot 10^{10}$ | 100       | $1.2 \cdot 10^9$ | A-2$^5$ |
|          | $\text{N}_2\text{O} + \text{H}_2\text{O} + e_{(\text{aq})}^- \rightarrow \text{N}_2 + \text{HO}^\bullet + \text{HO}^-$ | $9 \cdot 10^9$ | 24.8     | $2.2 \cdot 10^8$ | A-4$^5$ |
| H$^\bullet$ | $\text{S}_2\text{O}_8^{2-} + \text{H}^\bullet \rightarrow \text{SO}_4^{\bullet^+} + \text{SO}_4^{2-} + \text{H}^+$ | $1.4 \cdot 10^7$ | 10        | $1.4 \cdot 10^5$ | A-5$^6$ |
|          | $\text{P} + \text{H}^\bullet \rightarrow \text{P-H}$ | $1.95 \cdot 10^{10}$ | 1         | $1.95 \cdot 10^7$ | A-6$^7$ |
| SO$_4^{\bullet^-}$ | $\text{P} + \text{SO}_4^{\bullet^-} \rightarrow \text{P-H}^\bullet + \text{SO}_4^{2-}$ | $9 \cdot 10^8$ | 1         | $9 \cdot 10^5$ | 7$^8$    |

We optimized our reaction conditions to make sure our main products are $\text{^\bullet P-OH}$, reaction (1), and $\text{P^\bullet}$, 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 λ = 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 $T = 25^\circ\text{C}, 37^\circ\text{C}$ and $62^\circ\text{C}$ at pH=7 (Figure S4). Neutral pH was chosen for shifting the protolysis equilibrium towards the HO-adduct.

**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 N$_2$O 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 O$_2$, estimated experimentally.
3. Calibration of \([\text{Ce(III)}]\) and \([\text{Ce(IV)}]\) determinations

**Figure S6.** Absorption spectra of \(\text{Ce}_2(\text{SO}_4)_3\) in 0.1 M \(\text{H}_2\text{SO}_4\)

**Figure S7.** Absorption spectra of \(\text{CeSO}_4_2\) in 0.1 M \(\text{H}_2\text{SO}_4\)
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, \(\varepsilon = 0.66 \pm 0.01 \text{ mM}^{-1} \text{ cm}^{-1}\)

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, \(\varepsilon = 4.89 \pm 0.04 \text{ mM}^{-1} \text{ cm}^{-1}\)
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).

| Temperature (°C) | 2nd order rate constant $k_6$ (10⁵ M⁻¹ s⁻¹) |
|------------------|---------------------------------------------|
| 10               | 1.3                                         |
| 25               | 2.5                                         |
| 50               | 6.7                                         |
| 75               | 9.2                                         |
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 $r_{\text{HO}^\bullet}$

We need to identify a reasonable value for the rate of radical formation $r_{\text{HO}^\bullet}$ 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$^\bullet$ are expected to be much slower.\(^9\) Although the relative effectiveness of damage mitigation is independent of $r_{\text{HO}^\bullet}$ (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\(^\bullet\) 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.\(^10\) Considering two hydrogen fluoride (HF) molecules are emitted per attack of HO$^\bullet$, and using a membrane thickness of 50 µm, we obtain a rate of attack on the ionomer by HO$^\bullet$ in the range of $5\cdot10^{-6}$ to $5\cdot10^{-5}$ M·s$^{-1}$. However, in PFSA ionomer not all of the HO$^\bullet$ formed reacts with the polymer. Instead, a sizable fraction reacts with H$_2$ (at least near the anode side).\(^10\) If we estimate the probability of an attack of HO$^\bullet$ on the PFSA ionomer of 50%, the rate of formation of HO$^\bullet$ 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.\(^11,\ 12\) Therefore, we estimate the rate of HO$^\bullet$ formation in a hydrocarbon-based MEA to be in the range of $5\cdot10^{-7}$ to $5\cdot10^{-6}$ M·s$^{-1}$. In our simulation, we use a value of $r_{\text{HO}^\bullet} = 10^{-6}$ 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 $\tau = 0.1 \cdot [P] / r_{\text{HO}^\bullet} \approx 280$ 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.\(^11\)
6. Determination of model parameters

The model parameters \([P], [P-\text{SO}_3^-] = [\text{H}^+]\) and \([\text{H}_2\text{O}]\) 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, \(P-\text{SO}_3^-\), and protons, \(\text{H}^+\), is the same, because they are derived from the dissociation of sulfonic acid \(P-\text{SO}_3\text{H}\). We assume a density of the polymer in the dry state of \(\rho_{\text{pol}} = 1.2 \text{ g/cm}^3\) and a mass based water uptake of \(s = m_w / m_{\text{pol}} = 40 \%\). We can then estimate, under the assumption of a zero excess volume of mixing, the water volume fraction \(\Phi_w\):\(^{14}\)

\[
\Phi_w = \frac{V_w}{V_w + V_{\text{pol}}} = \frac{s}{s + \frac{\rho_w}{\rho_{\text{pol}}}}
\]

and obtain 32 \%, where we have used \(\rho_w = 1.0 \text{ g/cm}^3\). The concentration of water in the membrane is then \([\text{H}_2\text{O}] = 0.32 \cdot 55 \text{ mol/L} \cong 20 \text{ M}\). 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 \([P-\text{SO}_3^-]\) and \([\text{H}^+]\).

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

\[
\text{Scheme S1}
\]

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 \(\nu_{\text{tot}}\) of polymer with 1 mol of sulfonic acid groups and water:

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

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