Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Holistic approach to chemical degradation of Nafion membranes in fuel cells: modelling and predictions

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Supplementary Information

General scheme of the automatisation routine

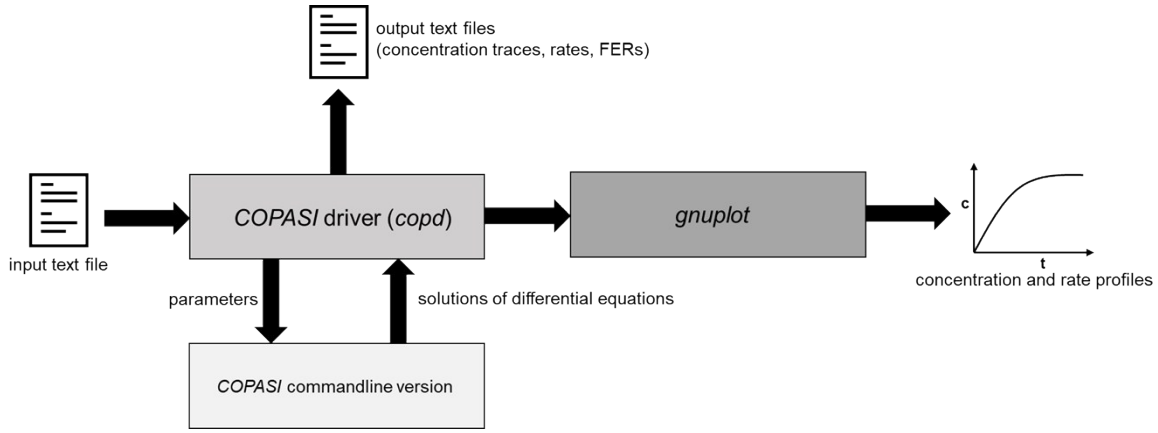

Fig. S1 Graphical representation of the automatisation routine.

Example for an input file

```
Model:
Degradation_Model_Nafion          # name of model (also default report file name)

Compartment:
Thickness: 50e-6                   # thickness of membrane in m

Constants: [T] = K, [A_n] = L/(mol*s), [A6] = s^(-1), [Ea_n] = J/mol
T = 368.15
A1 = 1.05e8
Ea1 = 35397
A2 = 8.43e18
Ea2 = 125520
A3 = 1.37e10
Ea3 = 9000
A4 = 2.74e13
Ea4 = 42000
A5 = 4.90e10
Ea5 = 33000
A6 = 1.00e13
Ea6 = 200832
A7 = 8.43e9
Ea7 = 14000
A8 = 2.71e6
```

```
Ea8 = 33472
A9 = 3.70e9
Ea9 = 20600
A10 = 1.33e11
Ea10 = 8000
A11 = 3.39e12
Ea11 = 14200
A12 = 9.14e10
Ea12 = 19246
A13 = 1.37e12
Ea13 = 10300
A14 = 6.80e18
Ea14 = 70000
A15 = 5.51e19
Ea15 = 70000
A16 = 1.56e20
Ea16 = 70000
A17 = 1.84e18
Ea17 = 70000
```

Functions:

```
Bi (more substrates): k1 * substrate1 * substrate2
```

Species: # all concentrations in mol/L

```
Fe2+,         1.79e-4
Fe3+,         0
H+,           0.01 fixed
H2,           1e-2, fixed
O2,           7.5e-3, fixed
H2O,          55.6
H2O2,         1e-3, fixed
H.,           0
OH.,          0
OOH.,         0
CO2,          0
HF,           0
SC-SO3H,      1.81
SC-O.,        0
HOCF2CF2SO3H,0
BB-O.,        0
(CF2)7COOH,   0
(CF2)6COOH,   0
(CF2)5COOH,   0
(CF2)4COOH,   0
(CF2)3COOH,   0
(CF2)2COOH,   0
(CF2)COOH,    0
COOH,         0
sum_COOH,     [(CF2)7COOH] + [(CF2)6COOH] + [(CF2)5COOH] + [(CF2)4COOH] + [(CF2)3COOH] +
[(CF2)2COOH] + [(CF2)COOH] + [COOH]
CFs,          [SC-SO3H] + [SC-O.]
CFm,          [SC-SO3H] + [SC-O.] + [BB-O.]
```

Reactions:

```
H2O2 + Fe2+ + H+ -> OH. + H2O + Fe3+,              Bi (more substrates),
k1 = A1 * exp(-Ea1 / (R * T))
H2O2 + Fe3+      -> OOH. + Fe2+ + H+,
k1 = A2 * exp(-Ea2 / (R * T))
```

```
Fe2+ + OH. + H+  -> Fe3+ + H2O,                    Bi (more substrates),
k1 = A3 * exp(-Ea3 / (R * T))
Fe2+ + OOH. + H+ -> Fe3+ + H2O2,                   Bi (more substrates),
k1 = A4 * exp(-Ea4 / (R * T))
Fe3+ + OOH.      -> Fe2+ + H+ + O2,
k1 = A5 * exp(-Ea5 / (R * T))
H2O2             -> 2 * OH.,
k1 = A6 * exp(-Ea6 / (R * T))
OH. + H2O2       -> OOH. + H2O,
k1 = A7 * exp(-Ea7 / (R * T))
OOH. + H2O2      -> OH. + H2O + O2,
k1 = A8 * exp(-Ea8 / (R * T))
2 * OOH.         -> H2O2 + O2,
k1 = A9 * exp(-Ea9 / (R * T))
2 * OH.          -> H2O2,
k1 = A10 * exp(-Ea10 / (R * T))
OOH. + OH.       -> H2O + O2,
k1 = A11 * exp(-Ea11 / (R * T))
OH. + H2         -> H. + H2O,
k1 = A12 * exp(-Ea12 / (R * T))
H. + O2          -> OOH.,
k1 = A13 * exp(-Ea13 / (R * T))
SC-SO3H + OH.    -> SC-O. + HOCF2CF2SO3H,
k1 = A14 * exp(-Ea14 / (R * T))
SC-O. + 3 * OH.  -> BB-O. + 6 * HF  + 3 * CO2,     Bi (more substrates),
k1 = A15 * exp(-Ea15 / (R * T))
BB-O. + OH.      -> 2 * (CF2)7COOH + 3 * HF,       Bi (more substrates),
k1 = A16 * exp(-Ea16 / (R * T))
(CF2)7COOH + 2 * OH. -> CO2 + 2 * HF + (CF2)6COOH, Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))
(CF2)6COOH + 2 * OH. -> CO2 + 2 * HF + (CF2)5COOH, Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))
(CF2)5COOH + 2 * OH. -> CO2 + 2 * HF + (CF2)4COOH, Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))
(CF2)4COOH + 2 * OH. -> CO2 + 2 * HF + (CF2)3COOH, Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))
(CF2)3COOH + 2 * OH. -> CO2 + 2 * HF + (CF2)2COOH, Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))
(CF2)2COOH + 2 * OH. -> CO2 + 2 * HF + (CF2)COOH,  Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))
(CF2)COOH + 2 * OH. -> CO2 + 2 * HF + COOH,        Bi (more substrates),
k1 = A17 * exp(-Ea17 / (R * T))


Task: # simulated time in seconds
3.6e5

Report:
C:\Users\...\Results\degradation_model_Nafion    # name of output file(s)
                                                 # must differ from all species!
# list of species to report on (default is all species that don't have a fixed
concentration)
Fe2+
Fe3+
#H+
#H2
#O2
#H2O
```

```
H2O2
H.
OH.
OOH.
CO2
HF
SC-SO3H
SC-O.
HOCF2CF2SO3H
BB-O.
(CF2)7COOH
(CF2)6COOH
(CF2)5COOH
(CF2)4COOH
(CF2)3COOH
(CF2)2COOH
(CF2)COOH
COOH
sum_COOH
CFs
CFm
```

Example for a graphical output

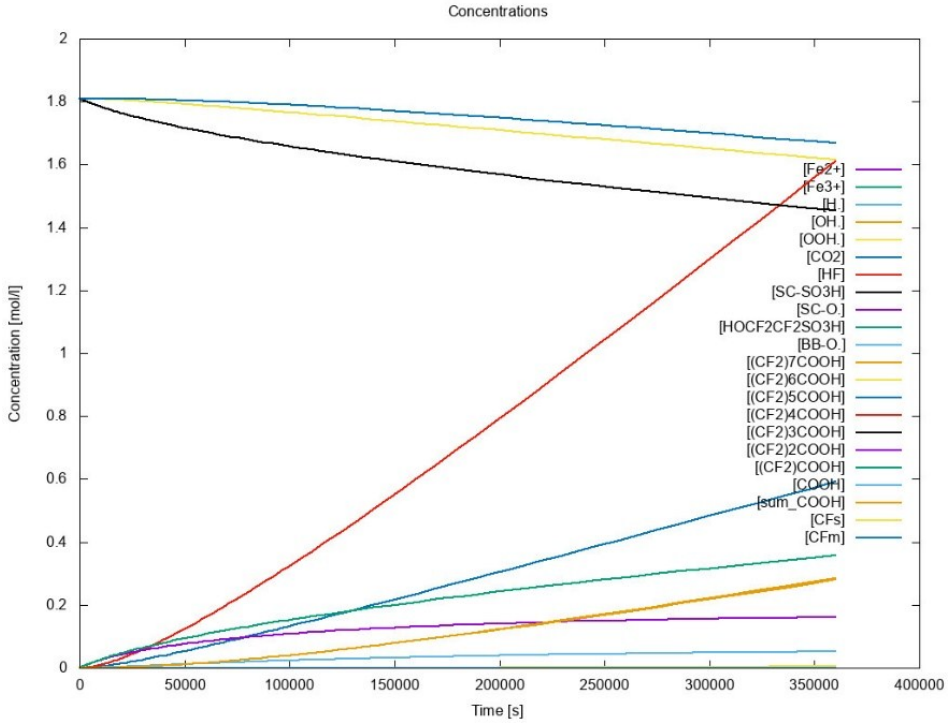

Fig. S2 Basic graphical outputs (jpg files) are generated by *copd* (via gnuplot) and allow a fast assessment of the data.

Fluoride emission rates

```
Time, FER, avg(FER)
0, 0
2.5e-10, 2.459646e-019, 3.196692e-019
5e-10, 1.2341142e-018, 8.2116e-019
8.98658e-10, 4.42269e-018, 1.72946883018901e-018
1.29732e-09, 9.236934e-018, 3.30062436407363e-018
1.69597e-09, 1.4876892e-017, 5.36975182344027e-018
2.09463e-09, 2.092356e-017, 7.76326320161556e-018
2.49329e-09, 2.71422e-017, 1.0369046520862e-017
2.89195e-09, 3.33999e-017, 1.31158284202701e-017
3.2906e-09, 3.96459e-017, 1.59543365951498e-017
3.68926e-09, 4.586886e-017, 1.88524636376943e-017
4.08792e-09, 5.20686e-017, 2.1790421534668e-017
4.48658e-09, 5.824818e-017, 2.47559477374749e-017
4.88523e-09, 6.441246e-017, 2.77409866065671e-017
5.28389e-09, 7.05654e-017, 3.07401024623904e-017
……
……
274082, 9.208674e-008, 7.64771126889033e-008
286204, 9.250506e-008, 7.71473494430546e-008
298326, 9.28917e-008, 7.77794091027936e-008
310448, 9.324918e-008, 7.83766041333815e-008
322571, 9.358038e-008, 7.89415043509801e-008
334693, 9.388764e-008, 7.94775510691888e-008
348483, 9.421074e-008, 8.00540628954641e-008
360000, 9.44604e-008, 8.0511e-008
```

Mathematica implementation of chemical reactor

Mathematica implementation of 0D chemical reactor is provided below. The notebook is separated into three main sections: In the first section, `(* INPUT OF MODEL PARAMETERS *)`, the user provides all relevant simulation parameters. Initial concentrations of relevant species are defined as: Fe^{2+} (`cFe2Init`) and Fe^{3+} ions (`cFe3Init`), hydrogen peroxide (`cH2O2Init`), radical species (`cHInit, cOHInit, cOOHInit`) and sulfonic acid head groups (`cSCSO3HInit`). The concentrations of oxygen (`cOxy`), hydrogen (`cHyd`) and protons (`cProt`) are kept constant during simulation, as well as temperature (`Temp`). The pre-exponential factors (`ASub`) and activation energies (`ESub`), and the target simulation time (`tMax`) are also defined in this section.
In the second section, `(* SOLUTION OF DIFFERENTIAL EQUATIONS *)` the inputs are processed and the differential equations are solved using Mathematica function `NDSolve[]`. The detailed function parameters can be freely adjusted by the user. The names of calculated variables are stored as list `VarsList`. The resulting time traces of concentrations are stored as Mathematica Interpolating functions in a variable `nds`.
In the third section, `(* PLOTTING OF RESULTS *)`, the concentration traces of all involved species are automatically plotted in a log-log scale.

```
(*INPUT OF MODEL PARAMETERS*)
(*Initial concentrations of relevant species [mol/l]*)
cFe2Init = 1.79*10^(-4);
cFe3Init = 0;
cH2O2Init = 10^-3;
cHInit = 0;
cOHInit = 0;
cOOHInit = 0;
cSCSO3HInit = 1.81;
```

```
(*Oxygen concentration [mol/l]*)
cOxy = 7.5*10^-3;
(*Hydrogen concentration [mol/l]*)
cHyd = 10*10^-3;
(*Proton concentration [mol/l]*)
cProt = 0.01;

(*Temperature [K]*)
Temp = 363.15;

(*Simulation time [s]*)
tMax = 100*3600;

(*MODEL PARAMETERS*)
(*Reaction rate constants A[L/mol/s]*)
ASub = {A1 -> 1.05`*^8, A2 -> 8.43`*^18, A3 -> 1.37`*^10, A4 -> 2.74`*^13, A5 -> 4.9`*^10, A6
-> 1.`*^13, A7 -> 8.43`*^9, A8 -> 2.71`*^6, A9 -> 3.7`*^9, A10 -> 1.33`*^11, A11 -> 3.39`*^12,
A12 -> 9.14`*^10, A13 -> 1.37`*^12, A14 -> 6.8`*^18, A15 -> 5.51`*^19, A16 -> 1.56`*^20, A17
-> 1.84`*^18};

(* Activation energies Esub [kJ/mol]*)
ESub = {E1 -> 35.397`, E2 -> 125.52`, E3 -> 9.`, E4 -> 42.`, E5 -> 33.`, E6 -> 200.832`, E7
-> 14.`, E8 -> 33.472`, E9 -> 20.6`, E10 -> 8.`, E11 -> 14.2`, E12 -> 19.246`, E13 -> 10.3`,
E14 -> 70.`, E15 -> 70.`, E16 -> 70.`, E17 -> 70.`};


(* SOLUTION OF DIFFERENTIAL EQUATIONS *)
(* number of variables*)
nVar = 19;

(*List of modelled species*)
VarsList = {cFe2, cFe3, cH2O2, cH, cOH, cOOH, cSCSO3H, cSCO, cBBO, cCF2COOH7, cCF2COOH6,
cCF2COOH5, cCF2COOH4, cCF2COOH3, cCF2COOH2, cCF2COOH1, cCF2COOH, cHF, cCO2};

(* Constant parameters *)
ParSub = {R -> 8.314*10^(-3), cH2 -> cHyd, cO2 -> cOxy, cHp -> cProt, T -> 363.15};

(* definition of reaction rates *)
k1 = A1*Exp[-E1/(R*T)]*cH2O2[t]*cFe2[t];
k2 = A2*Exp[-E2/(R*T)]*cH2O2[t]*cFe3[t];
k3 = A3*Exp[-E3/(R*T)]*cFe2[t]*cOH[t];
k4 = A4*Exp[-E4/(R*T)]*cFe2[t]*cOOH[t];
k5 = A5*Exp[-E5/(R*T)]*cFe3[t]*cOOH[t];
k6 = A6*Exp[-E6/(R*T)]*cH2O2[t];
k7 = A7*Exp[-E7/(R*T)]*cH2O2[t]*cOH[t];
k8 = A8*Exp[-E8/(R*T)]*cH2O2[t]*cOOH[t];
k9 = A9*Exp[-E9/(R*T)]*cOOH[t]*cOOH[t];
k10 = A10*Exp[-E10/(R*T)]*cOH[t]*cOH[t];
k11 = A11*Exp[-E11/(R*T)]*cOH[t]*cOOH[t];
k12 = A12*Exp[-E12/(R*T)]*cOH[t]*cH2;
k13 = A13*Exp[-E13/(R*T)]*cH[t]*cO2;
k14 = A14*Exp[-E14/(R*T)]*cSCSO3H[t]*cOH[t];
k15 = A15*Exp[-E15/(R*T)]*cSCO[t]*cOH[t];
k16 = A16*Exp[-E16/(R*T)]*cBBO[t]*cOH[t];
k17 = A17*Exp[-E17/(R*T)]*cCF2COOH7[t]*cOH[t];
k18 = A17*Exp[-E17/(R*T)]*cCF2COOH6[t]*cOH[t];
k19 = A17*Exp[-E17/(R*T)]*cCF2COOH5[t]*cOH[t];
```

```
k20 = A17*Exp[-E17/(R*T)]*cCF2COOH4[t]*cOH[t];
k21 = A17*Exp[-E17/(R*T)]*cCF2COOH3[t]*cOH[t];
k22 = A17*Exp[-E17/(R*T)]*cCF2COOH2[t]*cOH[t];
k23 = A17*Exp[-E17/(R*T)]*cCF2COOH1[t]*cOH[t];

(* Time derivatives of concentrations *)
dcFe2 = -k1 + k2 + 1*(-k3 - k4 + k5);
dcFe3 = k1 - k2 + 1*(k3 + k4 - k5);
dcH2O2 = 0; (*By default, constant peroxide concentration is assumed*)
(*dcH2O2=-k1-k2+k4-k6-k7-k8+k9+k10;*)   (*Uncomment this line to calculate peroxide
consumption*)
dcH = k12 - k13;
dcOH = k1 - k3 + 2*k6 - k7 + k8 - 2*k10 - k11 - k12 - k14 - 3*k15 - k16 - 2*k17 - 2*k18 -
2*k19 - 2*k20 - 2*k21 - 2*k22 - 2*k23;
dcOOH = k2 - k4 - k5 + k7 - k8 - 2*k9 - k11 + k13;
dcSCSO3H = -k14;
dcSCO = -k15 + k14;
dcBBO = -k16 + k15;
dcCF2COOH7 = 2*k16 - k17;
dcCF2COOH6 = k17 - k18;
dcCF2COOH5 = k18 - k19;
dcCF2COOH4 = k19 - k20;
dcCF2COOH3 = k20 - k21;
dcCF2COOH2 = k21 - k22;
dcCF2COOH1 = k22 - k23;
dcCF2COOH = k23;
dcHF = 6*k15 + 3*k16 + 2*k17 + 2*k18 + 2*k19 + 2*k20 + 2*k21 + 2*k22 + 2*k23;
dcCO2 = 3*k15 + k17 + k18 + k19 + k20 + k21 + k22 + k23;

(*List of initial values*)
initList = {cFe2Init, cFe3Init, cH2O2Init, cHInit, cOHInit, cOOHInit, cSCSO3HInit, 0, 0, 0,
0, 0, 0, 0, 0, 0, 0, 0, 0};

(* System of differential equations*)
ndSys = {(ToExpression[(ToString[#] <> "'[t]")] ==
        ToExpression[("d" <> ToString[#])]) & /@ VarsList,
    Table[(ToExpression[(ToString[VarsList[[i]]] <> "[0]")] ==
       initList[[i]]), {i, 1, nVar}]} // Flatten;

(* Solving the equations*)
nds = NDSolve[ndSys /. ParSub /. ESub /. ASub, VarsList, {t, 0, tMax}, AccuracyGoal -> 14,
PrecisionGoal -> 14];

(* PLOTTING OF RESULTS *)
(* Defining plot style *)
cols = {Black, Darker[Red, 0.3], Darker[Blue, 0.3], Orange, Darker[Green, 0.6], Purple,
Darker[Cyan, 0.3]};
cols21 = Flatten[{cols[[1 ;; 7]], {Dashed, #} & /@ cols[[1 ;; 7]], {Dotted, #} & /@ cols[[1
;; 7]]}, 1];

(* Plotting time traces in Log-Log scale *)
pltListMod = Table[LogLogPlot[VarsList[[i]][t] /. nds, {t, 10^-12, tMax}, PlotStyle ->
cols21[[i]], PlotRange -> All, PlotLabel -> VarsList[[i]], ImageSize -> 300], {i, 1, nVar}]
```

Comparison of *copd* and Mathematica results

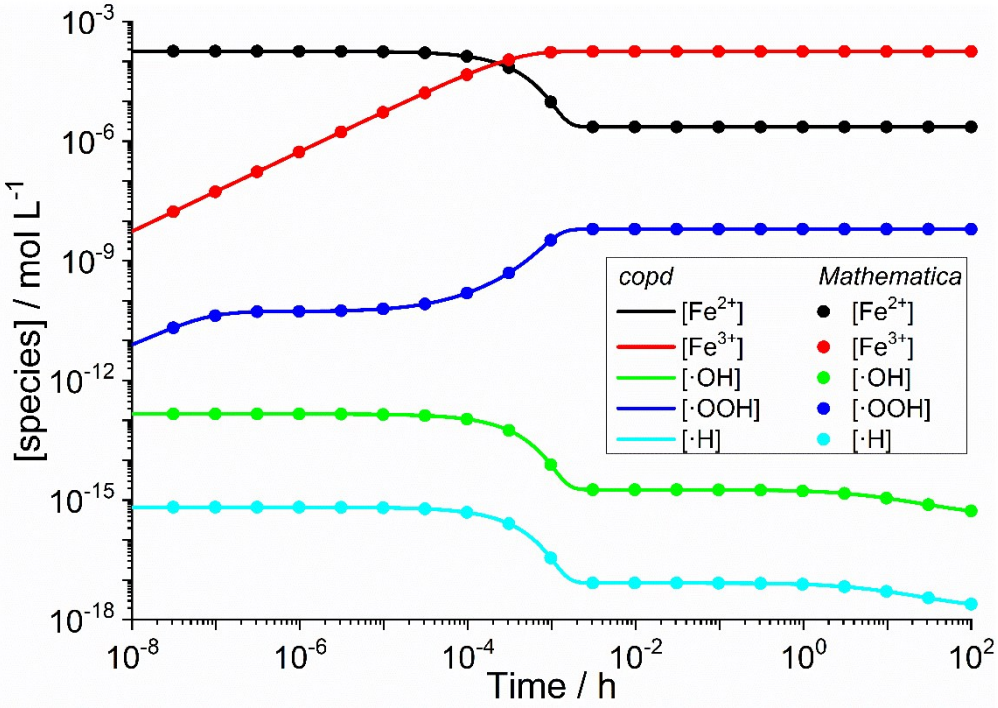

Fig. S3 Log-log plot of [Fe^{x+}] and radical concentrations as function of time for T = 363.15 K, [H_2O_2] = 1 mM, [$Fe^{2+}]_0$ = 10 ppm. The results obtained from *copd* are displayed as lines and the results obtained from Mathematica are shown as data points. For reasons of clarity, only every 50th data point of the Mathematica calculation (1001 data points) is depicted.

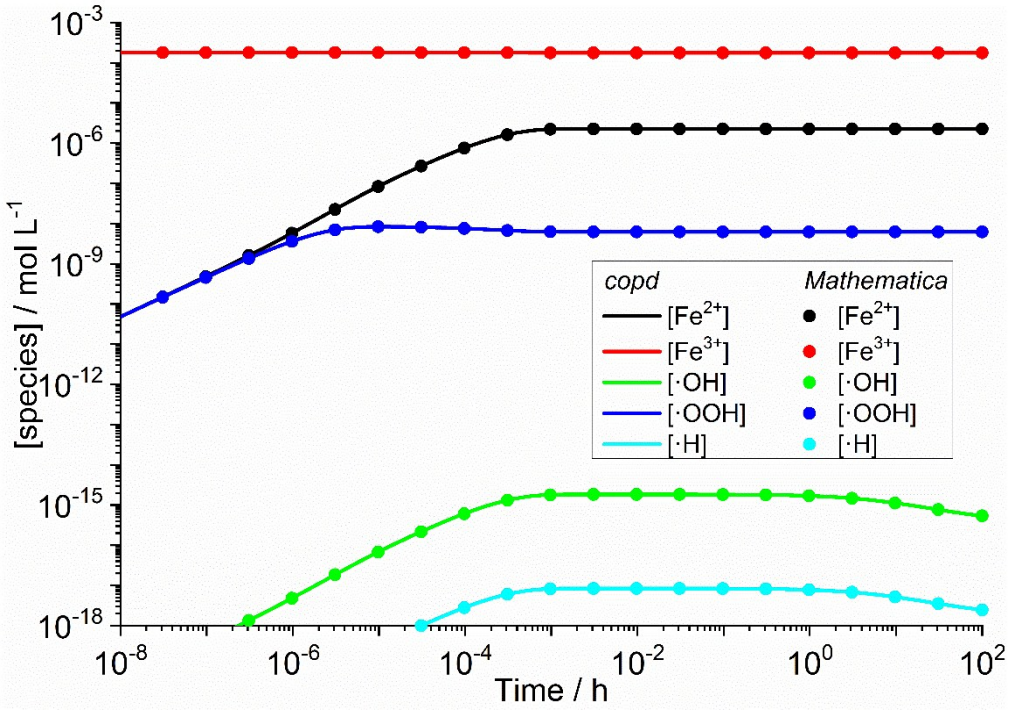

Fig. S4 Log-log plot of [Fe^{x+}] and radical concentrations as function of time for T = 363.15 K, [H_2O_2] = 1 mM, [$Fe^{3+}]_0$ = 10 ppm. The results obtained from *copd* are displayed as lines and the results obtained from Mathematica are shown as data points. For reasons of clarity, only every 50th data point of the Mathematica calculation (1001 data points) is depicted.

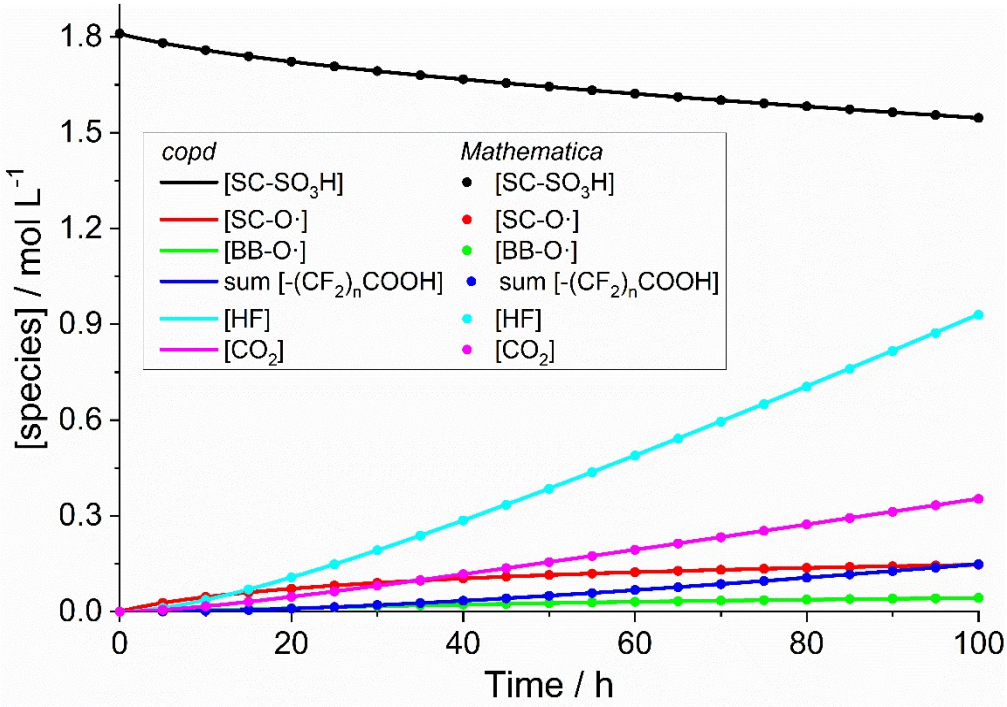

Fig. S5 Time traces of PFSA ionomer functional groups and degradation products for $[H_2O_2]$ = 1 mM, $[Fe^{2+}]_0$ = 10 ppm and T = 363.15 K. The results obtained from *copd* are displayed as lines and the results obtained from Mathematica are shown as data points. For reasons of clarity, only every 50th data point of the Mathematica calculation (1001 data points) is depicted.