

Polymer Electrolyte Fuel Cell Model

based on the work given in:

T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, J. Electrochem. Soc., 138, 2334 (1991)

This code uses the cubic approximation for the corrected diffusivity for all values of the water content.

It is more robust than the piecewise solution

```
> restart;
```

```
> with(plots):
```

```
> digits:=15;
```

```
digits := 15
```

```
> pars:={iapp=1.1,i0=0.01,Hflow=2,Oflow=3,Pa=3,Pc=3,tA=0.0365,
tC=0.0365,tMem=0.0175,Tcell=80,Tsat=80,Voc=1.1,xON=0.21,
xwA=0.1558,xwC=0.1558,PcO=49.8,PcH=12.8,PcN=33.5,PcW=217.7,
TcO=155,TcH=33.2,
TcN=126,TcW=647.096,e=0.5,MO=32,MW=18,MN=14,MH=2,F=96485,s=0.0126,
R=8.3145,xON=0.21,xIwA=0.1558,xIwC=0.1558};
```

```
pars := { F = 96485, MH = 2, MN = 14, MO = 32, MW = 18, Pa = 3, Pc = 3, PcH = 12.8,
PcN = 33.5, PcO = 49.8, PcW = 217.7, R = 8.3145, TcH = 33.2, TcN = 126, TcO = 155,
TcW = 647.096, Voc = 1.1, e = 0.5, i0 = 0.01, s = 0.0126, tA = 0.0365, tC = 0.0365, xON = 0.21,
xwA = 0.1558, xwC = 0.1558, Hflow = 2, Oflow = 3, Tcell = 80, Tsat = 80, iapp = 1.1,
tMem = 0.0175, xIwA = 0.1558, xIwC = 0.1558 }
```

Ratio of H2 supplied to H2 consumed

```
> nu[H]:=Hflow/iapp;
```

$$v_H := \frac{H_{flow}}{i_{app}}$$

Ratio of O2 supplied to O2 consumed

```
> nu[O]:=Oflow/iapp;
```

$$v_O := \frac{O_{flow}}{i_{app}}$$

- Diffusion Coefficients

Calculated from Equation 10

Diffusion Coefficient for water (vapor) and hydrogen gas

```
> DwH:=evalf(subs(pars,0.000364*(Tcell/(TcW*TcH)^(1/2))^(2.334)*(PcW
*PcH)^(1/3)*(TcH*TcW)^(5/12)*(1/MH+1/MW)^(1/2)*e^(3/2)/Pa));
```

```
DwH := 0.006989448527
```

Diffusion Coefficient for water (vapor) and oxygen gas

```
> DwO:=evalf(subs(pars,0.000364*(Tcell/(TcW*TcO)^(1/2))^(2.334)*(PcW
*PcO)^(1/3)*(TcO*TcW)^(5/12)*(1/MO+1/MW)^(1/2)*e^(3/2)/Pc));
```

```
DwO := 0.001367438403
```

Diffusion Coefficient for water (vapor) and nitrogen gas

```
> DwN:=evalf(subs(pars,0.000364*(Tcell/(TcW*TcN)^(1/2))^(2.334)*(PcW
```

```
*PcN)^(1/3)*(TcN*TcW)^(5/12)*(1/MN+1/MW)^(1/2)*e^(3/2)/Pc));
```

```
DwN := 0.001692835421
```

Diffusion Coefficient for oxygen and nitrogen gas

```
> DON:=evalf(subs(pars,0.0002745*(Tcell/(TcN*TcO)^(1/2))^(1.832)*(Pc
N*PcO)^(1/3)*(TcO*TcN)^(5/12)*(1/MO+1/MN)^(1/2)*e^(3/2)/Pc));
```

```
DON := 0.002714423430
```

[-] Governing Equations

Governing equation for mole fraction for water in the anode (Eq.11) (alpha is the ratio of water flux in the membrane to that produced in the cathode)

```
> Eq1:=diff(xwa(z),z)=R*Tcell*iapp/(2*F)/(Pa*DwH)*(xwa(z)*(1+alpha)-
alpha);
```

$$Eq1 := \frac{d}{dz} xwa(z) = \frac{71.53640205 R Tcell iapp (xwa(z) (1 + \alpha) - \alpha)}{F Pa}$$

Governing equation for mole fraction for oxygen in the cathode (Eq.12)

```
> Eq2:=diff(xO(z),z)=R*Tcell*iapp/(2*F)/Pc*((xO(z)*(1+alpha)+0.5*xwc
(z))/DwO+(1-xwc(z)-xO(z))/DON);
```

$$Eq2 := \frac{d}{dz} xO(z) = \frac{1}{2} R Tcell iapp$$

$$(731.2943660 xO(z) (1 + \alpha) - 2.7551779 xwc(z) + 368.4023609 - 368.4023609 xO(z)) / (F Pc)$$

Governing equation for mole fraction for water in the cathode (Eq.13)

```
> Eq3:=diff(xwc(z),z)=R*Tcell*iapp/(2*F)/Pc*((1-xwc(z)-xO(z))*(1+al
pha))/DwN+(0.5*xwc(z)+xO(z)*(1+alpha))/DON);
```

$$Eq3 := \frac{d}{dz} xwc(z) = \frac{1}{2} R Tcell iapp (590.7248794 (1 - xwc(z) - xO(z)) (1 + \alpha)$$

$$+ 368.4023609 xO(z) (1 + \alpha) + 184.2011804 xwc(z)) / (F Pc)$$

Mole fraction of water at cathode interface (Eq. 7)

```
> xw4:=subs(pars,(xIwC*nu[O]+2*(1+alpha)*(1-xIwC)*xON)/(nu[O]+(2*alp
ha+1)*(1-xIwC)*xON));
```

$$xw4 := \frac{0.7794730909 + 0.354564 \alpha}{2.904554727 + 0.354564 \alpha}$$

Mole fraction of oxygen at cathode interface (Eq. 7)

```
> xO4:=subs(pars,((nu[O]-1)*(1-xIwC)*xON)/(nu[O]+(2*alpha+1)*(1-xIwC
)*xON));
```

$$xO4 := \frac{0.3062143636}{2.904554727 + 0.354564 \alpha}$$

Mole fraction of water at anode interface (Eq. 8)

```
> xw1:=subs(pars,(nu[H]*xIwA-alpha*(1-xIwA))/(xIwA-alpha*(1-xIwA)+nu
```

[H]-1));

$$xwI := \frac{0.2832727272 - 0.8442 \alpha}{0.973981818 - 0.8442 \alpha}$$

Solve for the water mole fraction profile in the anode

> sol1:=subs(pars,dsolve({Eq1,xwa(0)=xw1}));

$$sol1 := xwa(z) = \frac{\alpha}{1 + \alpha} + e^{(0.1808276537(1 + \alpha)z)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right)$$

Solve for the water and oxygen mole fraction profile in the cathodes

> sol2:=evalf(subs(pars,dsolve({Eq2,Eq3,xwc(0)=xw4,xO(0)=xO4})));

> assign(sol1);

> assign(sol2);

Solve for water mole fraction at anode/membrane interface using above solution

> xw2:=(subs(z=tA,pars,xwa(z)));

$$xw2 := \frac{\alpha}{1 + \alpha} + e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right)$$

Solve for water mole fraction at cathode/membrane interface using above solution

> xw3:=subs(z=tC,pars,xwc(z));

Solve for oxygen mole fraction at cathode/membrane interface using above solution

> xO3:=(subs(z=tC,pars,xO(z)));

Saturation vapor pressure of water (Eq. 15)

> Psat:=subs(pars,10^(-2.1794+0.02953*Tsatsat-9.1837e-5*Tsatsat^2+1.4454e-7*Tsatsat^3));

$$Psat := 0.4669255941$$

Water vapor activity

> a:=(xw(z)*Pc/Psat);

$$a := 2.141668850 xw(z) Pc$$

Water content (# water molecules per charge site) in membrane when a<=1 (Eq. 16)

> lambda1:=(subs(pars,0.043+17.81*a-39.85*a^2+36*a^3));

$$\lambda1 := 0.043 + 114.4293667 xw(z) - 1645.036260 xw(z)^2 + 9548.237764 xw(z)^3$$

Water content in membrane when a>1 (Eq. 17)

> lambda2:=subs(pars,14+1.4*(a-1));

$$\lambda2 := 12.6 + 8.995009170 xw(z)$$

Water content at membrane/cathode interface

> lambdaxw3:=subs(xw(z)=xw3,pars,piecewise(a<=1,lambda1,a>1,lambda2));

Water content at membrane/anode interface

> lambdaxw2:=subs(xw(z)=xw2,pars,piecewise(a<=1,lambda1,a>1,lambda2));

$$lambdaxw2 := \left\{ 0.043 + \frac{114.4293667 \alpha}{1 + \alpha} \right.$$

$$+ 114.4293667 e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right) -$$

1645.036260

$$\left(\frac{\alpha}{1 + \alpha} + e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right) \right)^2 +$$

9548.237764

$$\left(\frac{\alpha}{1 + \alpha} + e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right) \right)^3,$$

$\frac{6.425006550 \alpha}{1 + \alpha}$

$1 + \alpha$

$$+ 6.425006550 e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right) \leq 1$$

$12.6 + \frac{8.995009170 \alpha}{1 + \alpha}$

$$+ 8.995009170 e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right), 1 <$$

$\frac{6.425006550 \alpha}{1 + \alpha}$

$1 + \alpha$

$$+ 6.425006550 e^{(0.006600209360 + 0.006600209360 \alpha)} \left(\frac{2(-118030303 + 351750000 \alpha)}{15(-54110101 + 46900000 \alpha)} - \frac{\alpha}{1 + \alpha} \right)$$

Number of water molecules per proton transferred

> **ndrag := 2.5 * lambda(z) / 22;**

$$ndrag := 0.1136363636 \lambda(z)$$

Assume Dprime is linear for lambda < 4. See Figure 3

> **Dprime := exp(2416 * (1/303 - 1/(273 + Tcell1))) * (a1 * lambda(z) + b1);**

$$Dprime := e^{\left(\frac{2416}{303} - \frac{2416}{273 + Tcell1} \right)} (a1 \lambda(z) + b1)$$

Solve for corrected diffusion coefficient for lambda less than 4 (Eq. 21)

> **Dlambda1 := subs(pars, (1/(1+s*lambda(z))^2 * lambda(z) / (a*(17.81 - 79.7*a + 108*a^2)))) * Dprime;**

$$Dlambda1 := \frac{0.1556418647 \lambda(z) e^{\left(\frac{2416}{303} - \frac{2416}{273 + Tcell1} \right)} (a1 \lambda(z) + b1)}{(1 + 0.0126 \lambda(z))^2 xw(z) (17.81 - 512.0730219 xw(z) + 4458.316590 xw(z)^2)}$$

Solve for corrected diffusion coefficient for lambda greater than 4 (Eq. 22)

> **Dlambda4 := evalf(subs(pars, 1e-6 * exp(2416 * (1/303 - 1/(273 + Tcell1))) * (2.563 - 0.33 * lambda(z) + 0.0264 * lambda(z)^2 - 0.000671 * lambda(z)^3)));**

Dlambda4 :=

$$0.1 \cdot 10^{-5} e^{\left(7.973597360 - \frac{2416.}{273. + T_{cell1}}\right)} (2.563 - 0.33 \lambda(z) + 0.0264 \lambda(z)^2 - 0.000671 \lambda(z)^3)$$

Solve for the coefficients for Dprime by assuming the corrected diffusion coefficient is continuous at Dlambda=4, and Dprime=0.6e-6 at lambda=2 and T=30 deg

> use RealDomain in

```
Temp:=solve({4=lambda1,subs(lambda(z)=4,Tcell1=30,Dlambda1)=subs(lambda(z)=4,Tcell1=30,Dlambda4),subs(lambda(z)=2,Tcell1=30,Dprime)=0.6e-6},{xw(z),a1,b1}) end use;
```

Temp := { a1 = 0.7357235260 10⁻⁶, b1 = -0.8714470520 10⁻⁶, xw(z) = 0.09044297269 }

Solve for the water mole fraction in terms of water content in the separator-- since Eq. 16 is cubic, the solution is limited to the real solution

This ensures that the water content (lambda(z)) is the only dependent variable

```
> use RealDomain in Temp1:=solve({lambda(z)=lambda1},{xw(z)}) end use;
```

```
Temp1 := { xw(z) = 0.1024000000 10-33 (0.2022301 107 (-0.1767584599 1080
+ 0.5896706604 1079 lambda(z) +
0.5489512422 1074 sqrt(0.1051024347 1012 - 0.6917547978 1011 lambda(z) + 0.1153855687 1011 lambda(z)2)(2/3)
- 0.3285467212 1059 + 0.5608297441 1033 (-0.1767584599 1080 + 0.5896706604 1079 lambda(z)
+
0.5489512422 1074 sqrt(0.1051024347 1012 - 0.6917547978 1011 lambda(z) + 0.1153855687 1011 lambda(z)2)(1/3)
) / (-0.1767584599 1080 + 0.5896706604 1079 lambda(z) +
0.5489512422 1074 sqrt(0.1051024347 1012 - 0.6917547978 1011 lambda(z) + 0.1153855687 1011 lambda(z)2)(1/3)
) }
```

```
> a1:=subs(Temp,a1);b1:=subs(Temp,b1);
```

a1 := 0.7357235260 10⁻⁶

b1 := -0.8714470520 10⁻⁶

```
> Dlambda1:=subs(Temp1,Tcell1=Tcell,pars,Dlambda1):Dlambda4:=subs(Tcell1=Tcell,pars,Dlambda4):
```

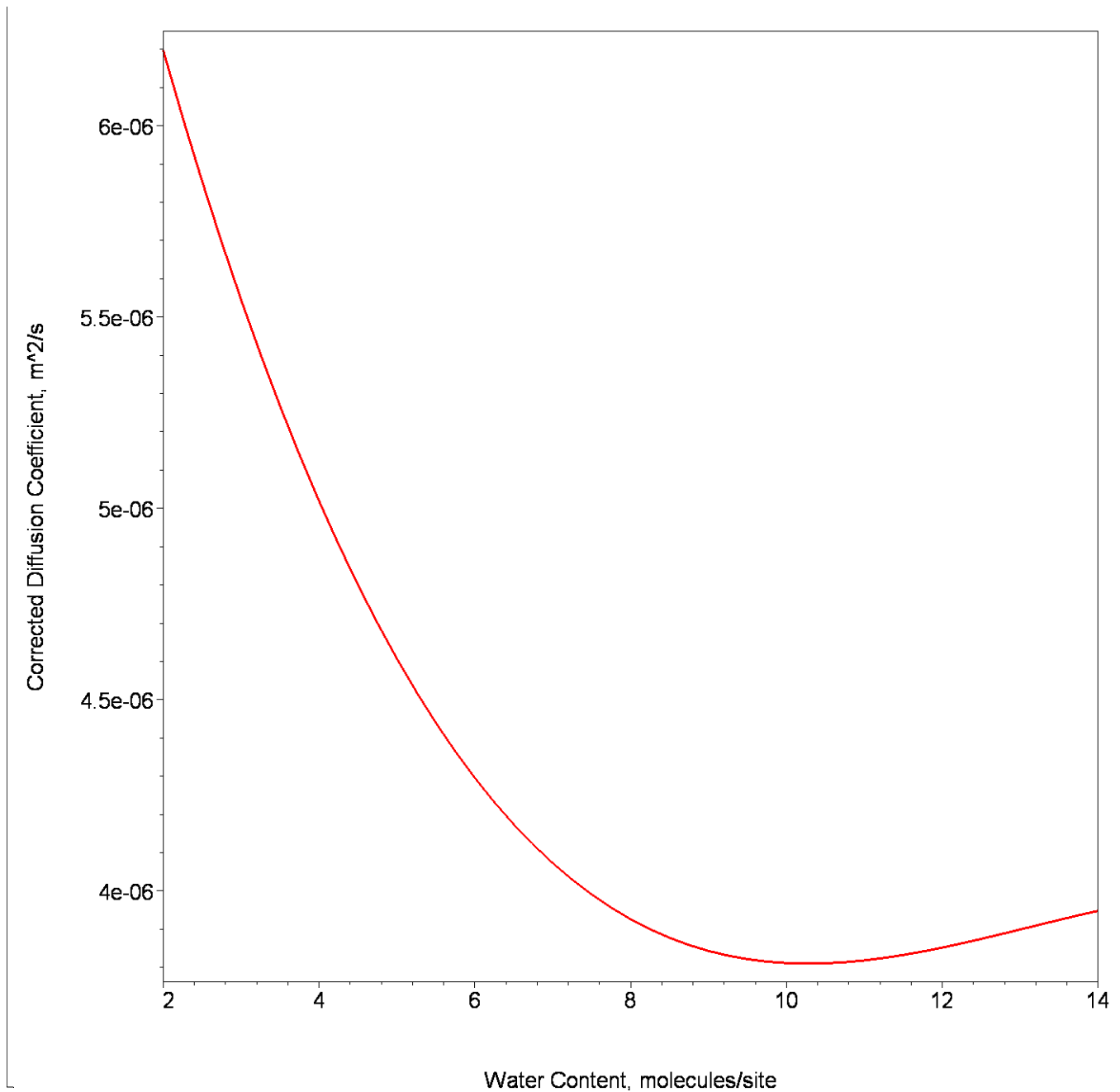
>

Total corrected diffusion coefficient--use cubic representation for entire domain

```
> Dlambda:=Dlambda4:
```

Plot of corrected diffusion coefficient with lambda

```
> plot(subs(lambda(z)=y,Dlambda),y=2..14,axes=boxed,thickness=3,labels=["Water Content, molecules/site","Corrected Diffusion Coefficient, m^2/s"],labeldirections=[Horizontal, Vertical]);
```



```

Governing equation for water content in the membrane
> Eq4:=subs(pars,diff(lambda(z),z)=(2*ndrag-alpha)*(iapp/(2*F))*1155
  /(1*Dlambda)):
[ >
Solve for water content in the membrane as a function of alpha
> soltest:=dsolve({Eq4,lambda(0)=lambdaxw2},numeric,parameters=[alpha],abserr=1e-12):
[ >

```

- Determine alpha

[Solves for alpha so that the water content calculated at the anode/membrane interface as calculated by

sol1 above (lambdaxw3) agrees with water content calculated by soltest.

If solution fails, try a different initial alpha guess

```
> #alphaguess:=subs(fsol,alpha);
  alphaguess:=0.8:
  errout:=1:
  soltest('parameters'=[alphaguess]):
  soltest(subs(pars,tMem)):
  evalf(subs(alpha=alphaguess,lambdaxw3)):
  err:=evalf(rhs(soltest(subs(pars,tMem))[2])-subs(alpha=alphaguess,
  lambdaxw3));
  while errout>1e-5 do
  soltest('parameters'=[1.000001*alphaguess]):
> derr1:=(evalf(rhs(soltest(subs(pars,tMem))[2])-subs(alpha=1.000001
  *alphaguess,lambdaxw3))):
  soltest('parameters'=[0.999999*alphaguess]):
> derr2:=(evalf(rhs(soltest(subs(pars,tMem))[2])-subs(alpha=0.999999
  *alphaguess,lambdaxw3))):
  derr:=(derr1-derr2)/(2*0.000001*alphaguess);
  alphaguessnew:=alphaguess-err/derr;
  cont:=true:

  while cont=true do
  s11:='s11':
  try
  soltest('parameters'=[alphaguessnew]);
  s11:=evalf(rhs(soltest(subs(pars,tMem))[2])-subs(alpha=alphaguessn
  ew,lambdaxw3));
  catch:
  end try:

  if is(s11,numeric)=true then

  err:=s11:
  alphaguess:=alphaguessnew:
  cont:=false:
  else
  alphaguessnew:=(alphaguess+alphaguessnew)/2:
  print(alphaguessnew);
  cont:=true:
  end:
  end:
```

```
errout:=sqrt(err^2):
print(subs((soltest(subs(pars,tMem)),lambda(z))),evalf(subs(alpha=
alphaguess,lambdaxw3)),errout);
```

```
end:
```

```
err := -25762.36545
-9673.92840341358534, 15.83960628, 9689.768009
-3536.04893357864012, 15.78097265, 3551.829907
-1251.52741516936726, 15.72230824, 1267.249723
-425.576980772131662, 15.66666021, 441.2436410
-136.399927080999276, 15.61625187, 152.0161790
-40.6736006111127466, 15.57106467, 56.24466528
-13.4069651585272461, 15.52020954, 28.92717470
0.2871909917
0.3179433801
0.3333195743
-9.32844892112161794, 15.50671148, 24.83516040
0.2969884570
0.3151540157
0.3242367950
-4.31049067196994429, 15.49871853, 19.80920920
0.3150857065
0.3196612507
0.3219490229
-0.289578669590607738, 15.49670209, 15.78628076
0.3193995866
0.3206743047
8.22166800458876246, 15.49557864, 7.273910635
16.8992506782473910, 15.49511092, 1.404139760
15.5217342592018498, 15.49517646, 0.02655780000
15.4951872845648656, 15.49517748, 0.9800000000 10-5
```

```
> asol:=alpha=alphaguess;
```

```
asol :=  $\alpha = 0.3202214166$ 
```

```
Water profile in anode
```

```
> xwa(z):=subs(asol,xwa(z));
```

```
xwa(z) :=  $0.2425512967 - 0.2241589272 e^{(0.2387325412 z)}$ 
```

```
Water profile in cathode
```

```
> xwc(z):=subs(asol,xwc(z));
```


$$xwc(z) := -0.17552346 e^{(0.7554822157 z)} - 1.138181891 e^{(-0.7537359479 z)} + 1.6095915$$

Oxygen profile in cathode

```
> xO(z) := subs(asol, xO(z));
```

$$xO(z) := 0.7136786501 e^{(0.7554822157 z)} - 0.002627626110 e^{(-0.7537359479 z)} - 0.6095914956$$

Conductivity

```
> sigma30 := 0.005139 * lambda(z) - 0.00326;
```

$$\sigma_{30} := 0.005139 \lambda(z) - 0.00326$$

```
> sigma := evalf(subs(pars, exp(1268 * (1/303 - 1/(273 + Tcell))) * sigma30));
```

$$\sigma := 0.009296230552 \lambda(z) - 0.005897200156$$

```
> lambda[0] := rhs(soltest(0)[2]);
```

$$\lambda_0 := 1.52139262997814$$

```
> Nstep := 999;
```

```
h := subs(pars, tMem / (Nstep + 1));
```

```
hC := subs(pars, tC / (Nstep + 1));
```

```
hA := subs(pars, tA / (Nstep + 1));
```

$$h := 0.00001750000000$$

$$hC := 0.00003650000000$$

$$hA := 0.00003650000000$$

```
> xcoord := seq(n, n = 0 .. Nstep + 1);
```

Discretize behavior in the membrane to determine membrane resistance--this is needed due to the piecewise functions involved

```
> for j from 0 to Nstep + 1 do
```

```
  lambda[n][j] := rhs(soltest(j * h)[2]);
```

```
  #print(lambda[n][j]);
```

```
  if lambda[n][j] < 14 then
```

```
    EqX := lambda[n][j] = subs(pars, 0.043 + 17.81 * a - 39.85 * a^2 + 36 * a^3);
```

```
    xwm[j] := solve(EqX, xw(z))[1];
```

```
  else
```

```
    EqX := lambda[n][j] = subs(pars, 14 + 1.4 * (a - 1));
```

```
    xwm[j] := solve(EqX, xw(z));
```

```
  end;
```

```
xwcat[j] := subs(z = (Nstep + 1 - j) * hC, xwc(z));
```

```
xwan[j] := subs(z = (j) * hA, xwa(z));
```

```
xOx[j] := subs(z = (Nstep + 1 - j) * hC, xO(z));
```

```
sig[j] := subs(lambda(z) = lambda[n][j], sigma);
```

```
dR[j] := 1 / sig[j];
```

```
od;
```

Membrane resistance (Eq. 26)

```
> Rm := evalf((2 * sum(subs(z = 2 * k * h, dR[2 * k]), k = 1 .. (Nstep + 1) / 2 - 1) + (4 * sum(
  subs(x = (2 * k - 1) * h, dR[2 * k - 1]), k = 1 .. ((Nstep + 1) / 2)) + (subs(x = 0, dR[0]) +
```

```
subs(x=1,dR[Nstep+1])))*h/(3);
```

```
Rm := 1.126905095
```

```
> xO3:=evalf(subs(z=tC,pars,xO(z)));
```

```
xO3 := 0.1214844405
```

Equation for voltage of the fuel cell for a given applied current

```
> EqV:=subs(pars,iapp=i0*Pc*xO3*exp(0.5*F/(R*Tcell)*(Voc-Vcell-Rm)))
```

```
;
```

```
EqV := 1.1 = 0.003644533215 e(-1.951363650 - 72.52766250 Vcell)
```

```
> Vcell:=solve(EqV,Vcell);
```

```
Vcell := -0.1056314315
```

```
>
```

Plot the water mole

```
> p1:=plot([xcoord*hA],[seq(xwan[n],n=0..Nstep+1)]):
```

```
p2:=plot([seq(xcoord[n]*h+hA*(Nstep+1),n=1..Nstep+2)],[seq(xwm[n],
```

```
n=0..Nstep+1)]):
```

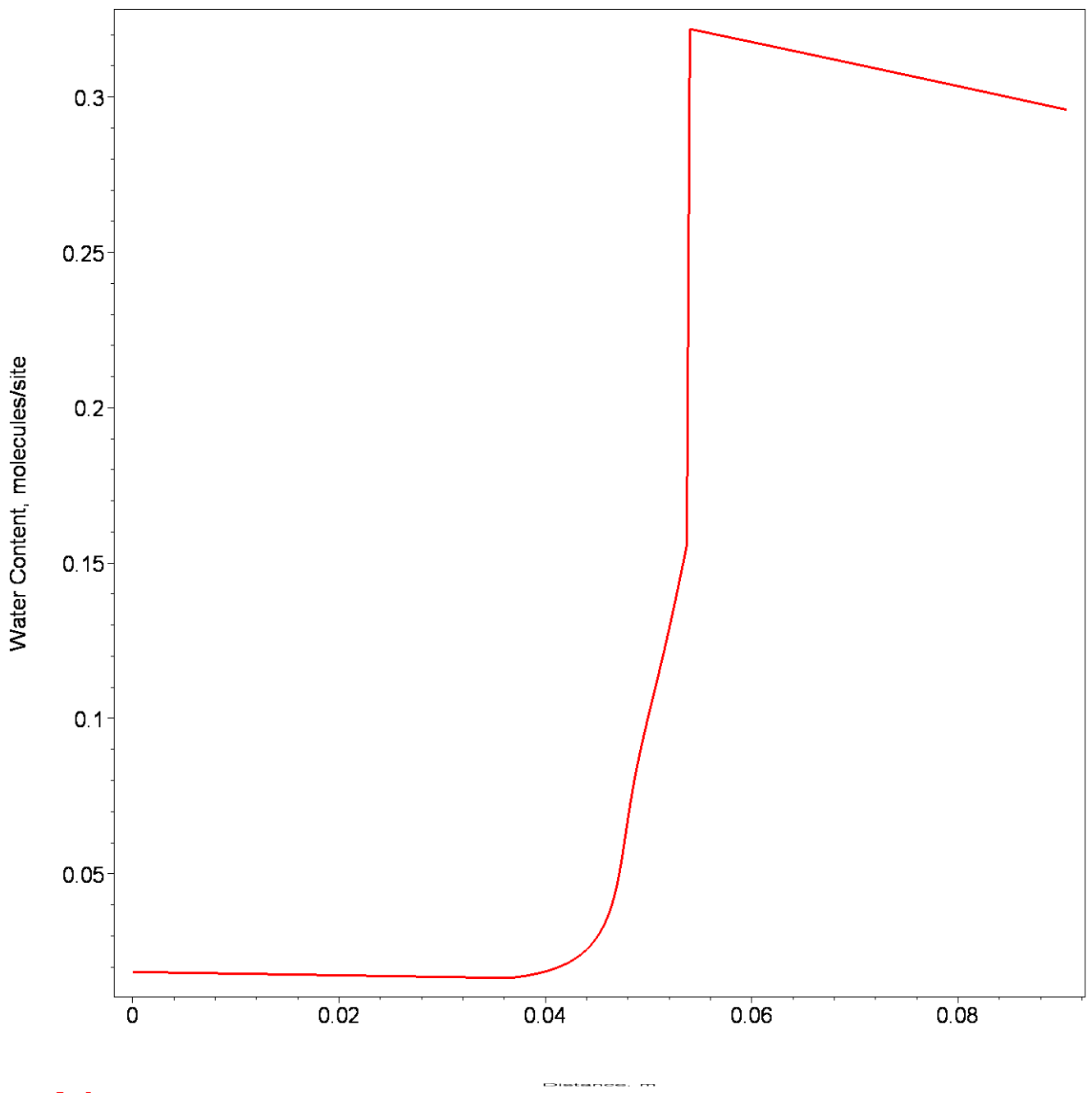
```
p3:=plot([seq(xcoord[n]*hC+(h+hA)*(Nstep+1),n=1..Nstep+2)],[seq(xw
```

```
cat[n],n=0..Nstep+1)]):
```

```
> display({p1,p2,p3},axes=boxed,thickness=3,labels=["Distance, m",
```

```
"Water Content, molecules/site"],labeldirections=[Horizontal,
```

```
Vertical]);
```



> **alphaguess;**

0.3202214166

> **Rm;**

1.126905095

If Vcell<0, the fuel cell cannot provide the required current

> **vcell;**

-0.1056314315