Monash Electrochemistry Simulator (MECSim)

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Overview

- Why use it?
- Installing
- Compiling and running
- Editing parameters
- Recent changes: treatment of iR effect
- Test of iR effect

Motivation

- Free software
- Tested against DigiSim
- Can include multiple sinusoids (unlike DigiSim)
- Allows for complicated DC ramp parameters
- Includes any number of charge transfer (A + e = B), catalytic (B = C) and chemical (A + B = C + D) reactions
- Output files in “DigiPot” format

Installation

- Install “CygWin” so similar Linux emulation software which supports Fortran 77 (freeware available from http://www.cygwin.com/)
- Make sure these are added when you install (check “gcc-g77” under “Devel”)
- Additional documentation on this exists and is available on request

Compiling and running MECSim

- Extract files from zip (available on request) to desired directory. Will assume this is "c:/directoryname" here
- Start "CygWin" (e.g. from icon on desktop)
  - Type "cd /cygwin/c/directoryname"
  - Type "./compile" if this is the first time
    - To run type "./MECSim.exe"

- Screen should look similar to this

```
/cygdrive/c/DirectoryName

Owner@HAL ~
$ cd /cygdrive/c/DirectoryName/

Owner@HAL /cygdrive/c/DirectoryName
$ ./compile

Owner@HAL /cygdrive/c/DirectoryName
$ ./MECSim.exe
```

and after you hit enter…

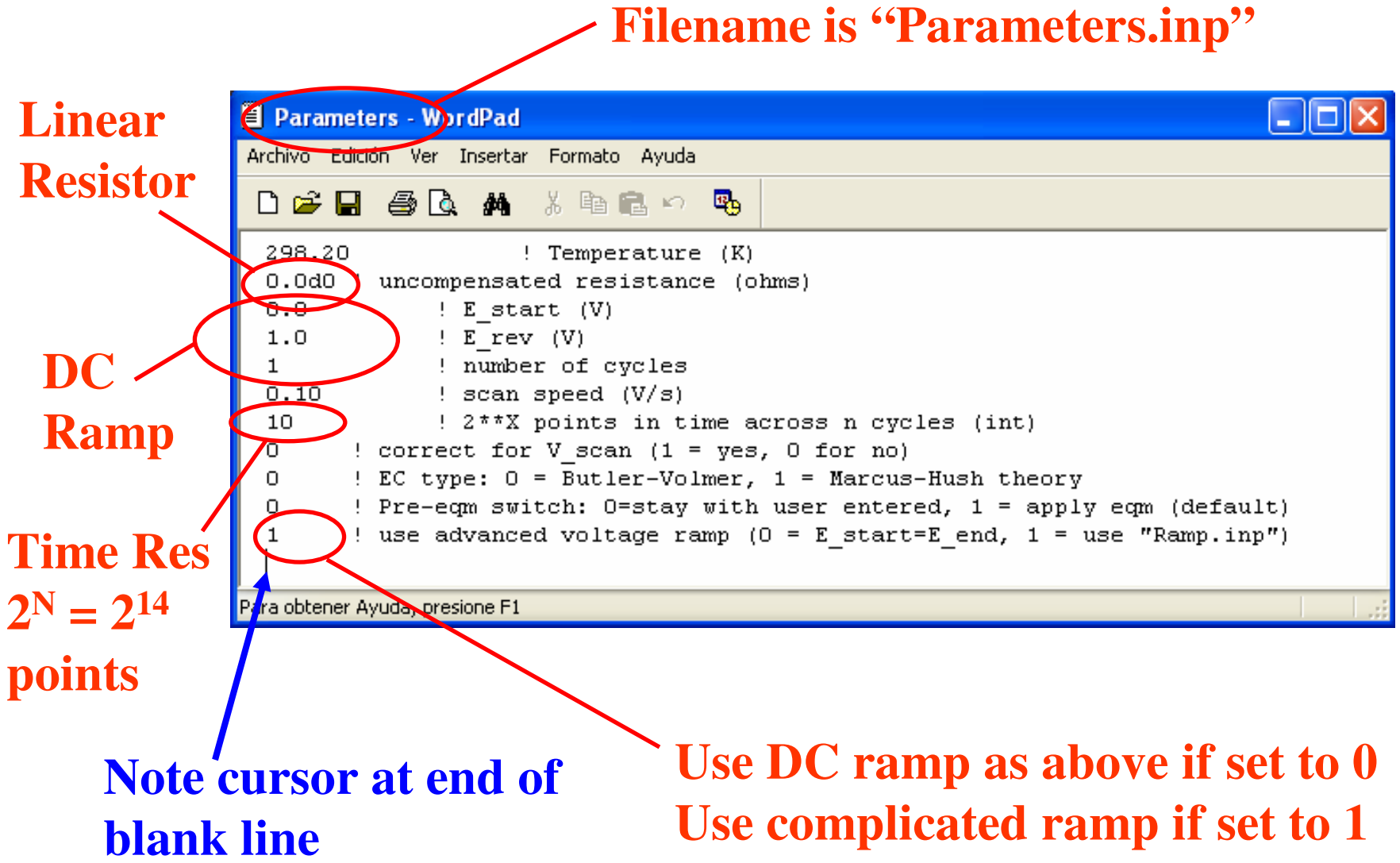
```
Done  90%; t,Eapp,i =    0.12E+02   0.31E+00   0.70E-06,   C_err= -0.18E-11
Done 100%; t,Eapp,i =    0.13E+02   0.50E+00   0.61E-06,   C_err= -0.20E-11

 ************************************************************

 Current min/max (A) =  -1.10010663E-05  1.04942881E-05

 Average number of iterations at electrode surface =   10.2367554
 Average number of iterations for second order chem =   1.
 Maximum number of iterations used at electrode =  1000

DEC_Model.txt: done.
 Final Concs at mt, time, Eapp= 16384  13.4217728  0.500170898
 C 1 =   0.999968445  0.999295468  0.997322327!  0.99998598
 C 2 =   3.1555494E-05  0.000704531833  0.00267767312!  1.40200939E-05

 C_err (=0 if Diff equal) =  -2.03156375E-12 -2.03156375E-12 -2.03144733E-12!
  3.67523165E-13


 Output file written to DEC_Model.txt
```

Output file (DigiPot format)

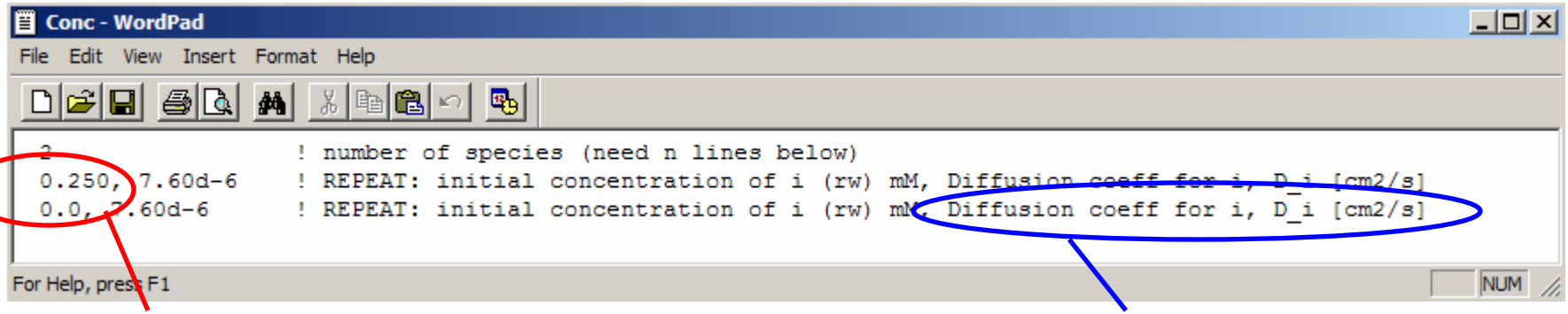
Editing parameters

- Not really a general purpose simulator if you can't change the parameters
- All input files are text format with extension *.inp
- Cautionary note: make sure all *.inp files end in a blank line (Fortran thing)

Editing general simulation parameters



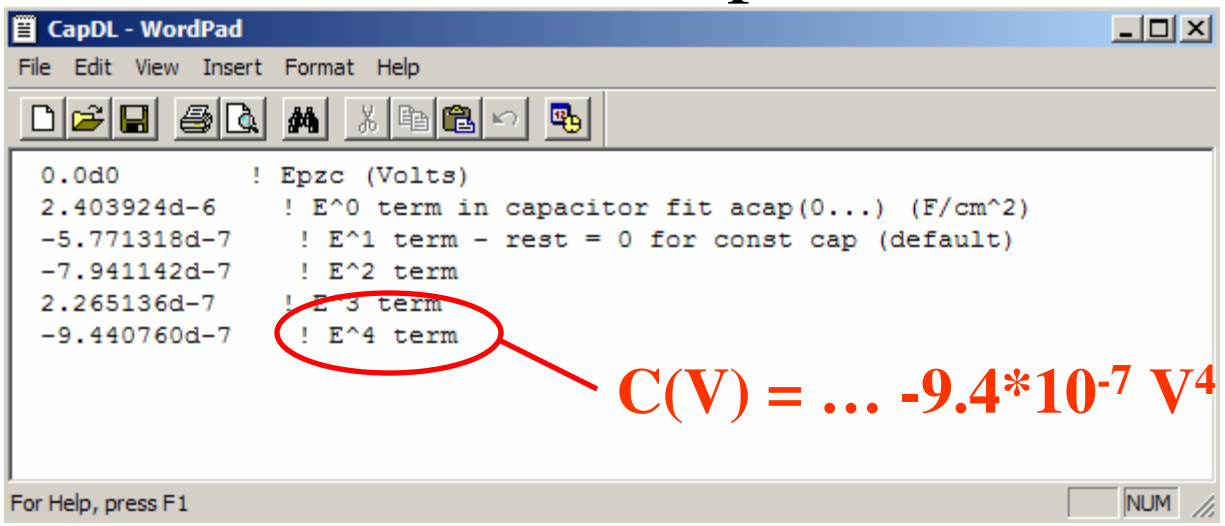
Concentrations



Total number of active species
(make sure there are the same number of lines following)

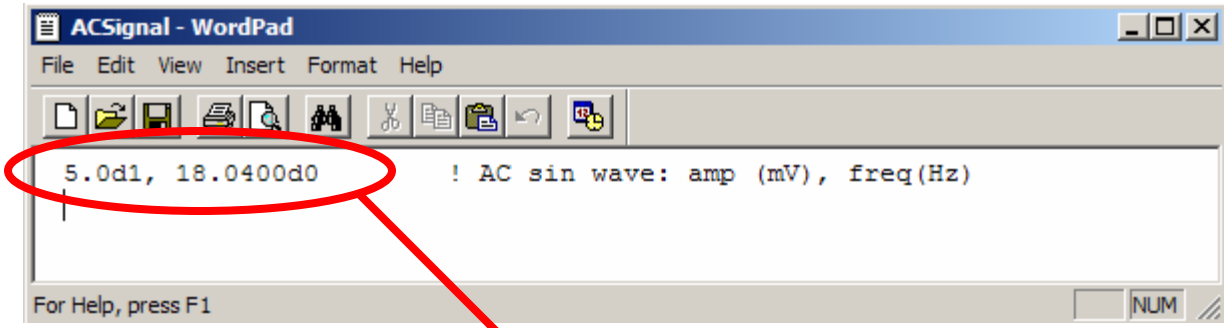
Diffusion coefficient

Non-linear capacitor



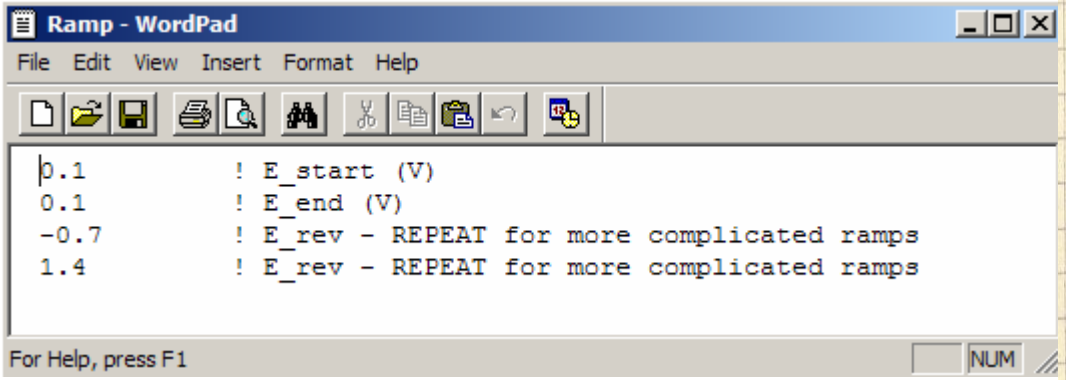
C(V) = … $-9.4*10^{-7}$ V^4 (F/cm^2)

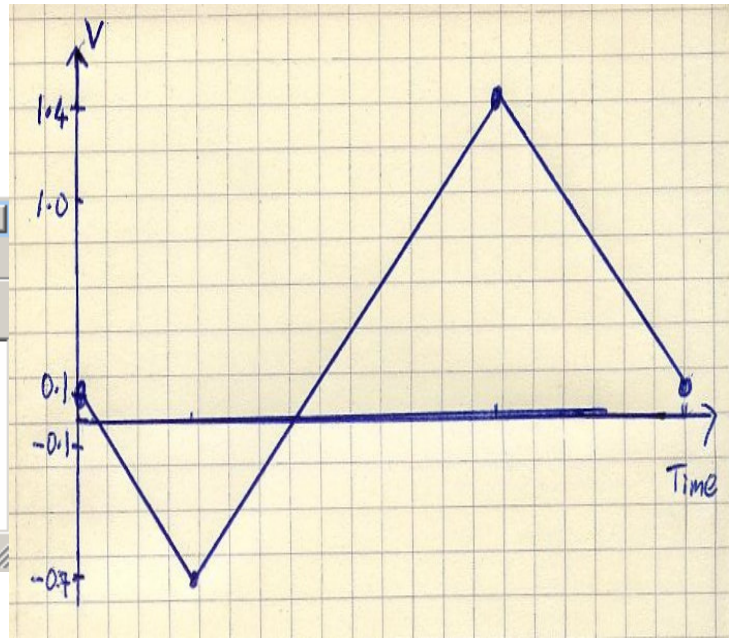
AC Signal added to DC ramp



Sinusoid of 50mV @ 18.04Hz

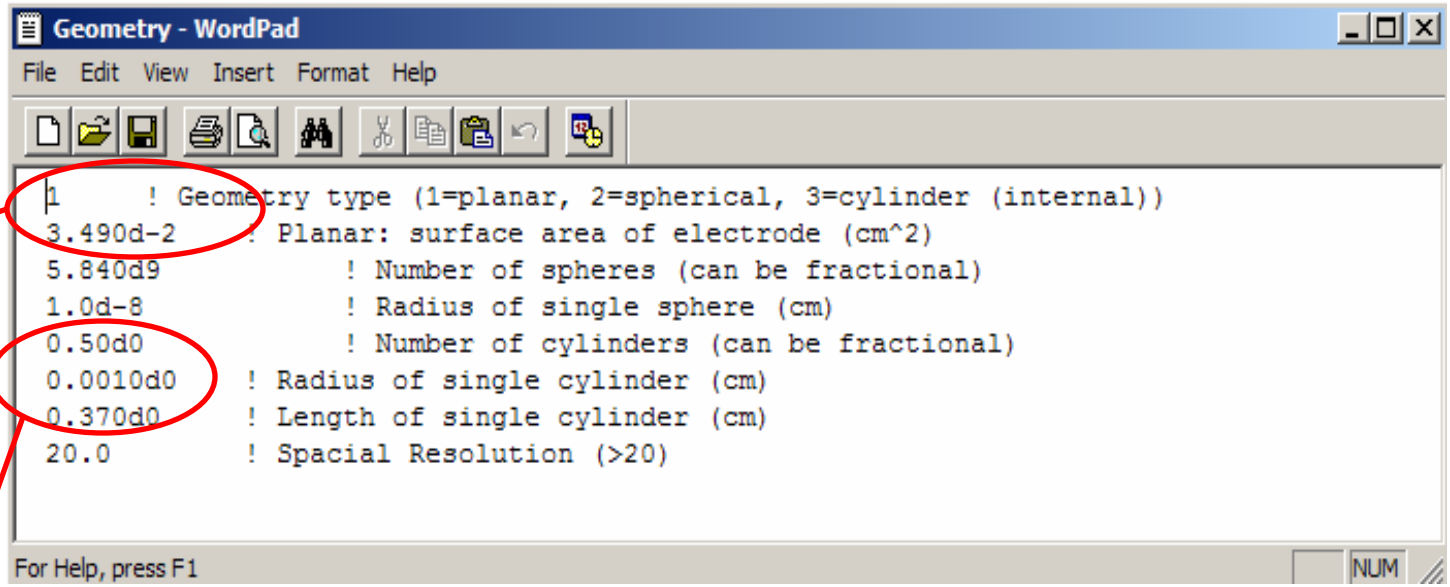
More complicated DC ramp





Electrode surface geometry

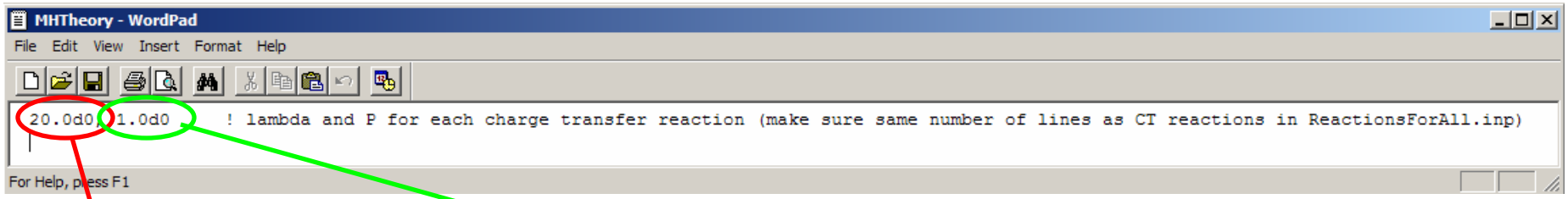
Standard
0.00349cm^2



If type set to 3 then uses ½ of a cylinder (hemi-cylinder) of length 0.37cm and radius 10μm

Marcus-Hush Theory

Switched on in Parameters.inp



λ^* is a scaled quantity given by $\lambda^* = \lambda / (k_b T)$ where λ is the solvent reorganisation energy

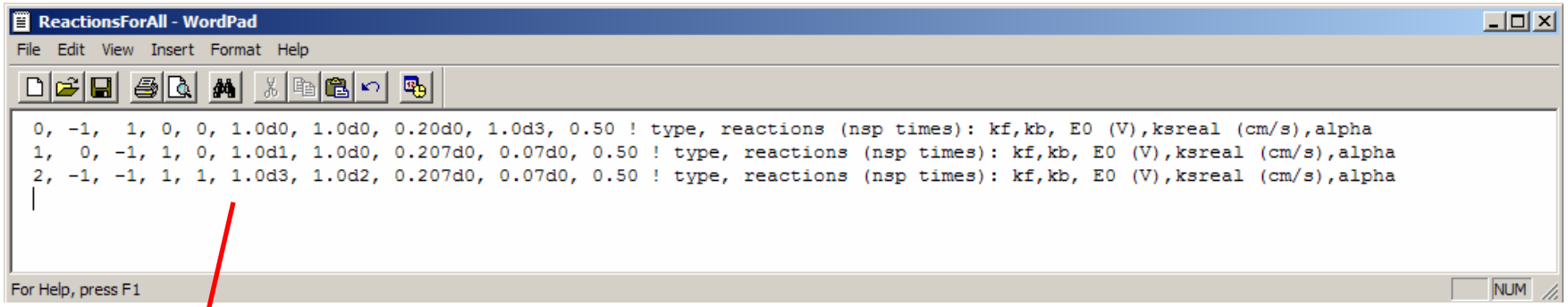
P is a constant dependent on the type of electrode

For more information on the physical definitions of P and λ refer to Steve Feldberg's lecture series given at Monash University over February and March 2008.

Format of reactions input file

Mechanism:

- $A + e = B$; $E^0 = 0.2V$, $k_s = 1000$ cm/s, $\alpha = 0.5$
- $B = C$; $k_f = 10$, $k_b = 1$
- $A + B = C + D$; $k_f = 1000$, $k_b = 100$

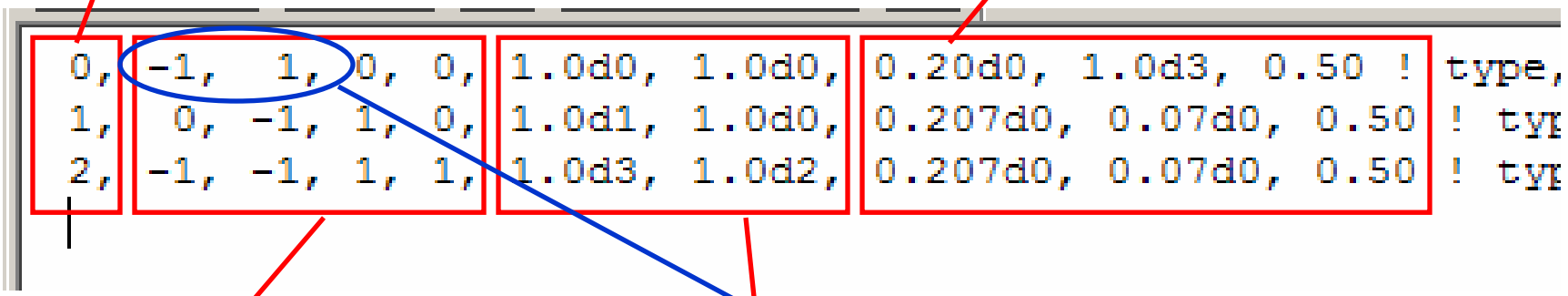


One line per reaction

Reactions input file (cont.)

Reaction type: 0 = charge transfer, 1 = catalytic, 2 = chemical

CT parameters: E^0, k_s, α (ignored by chem)



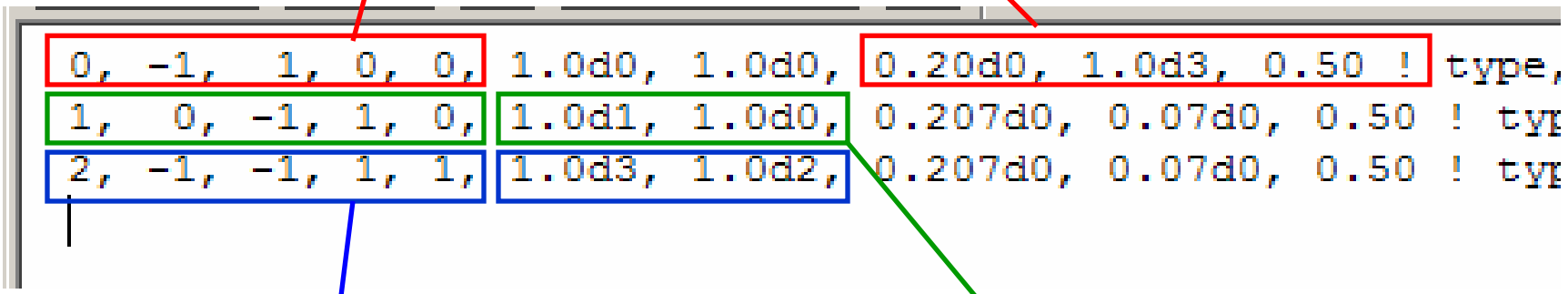
Reation matrix: note that the number of columns must equal the number of concentrations

-1 is left of reaction, +1 is right hand side (0 is not involved). So this translates to: A + e = B

Forward/Backward rates (ignored by CT)

Reactions input file (cont.)

CT: A + e = B; E^0 = 0.2V, k_s = 1000 cm/s, α = 0.5



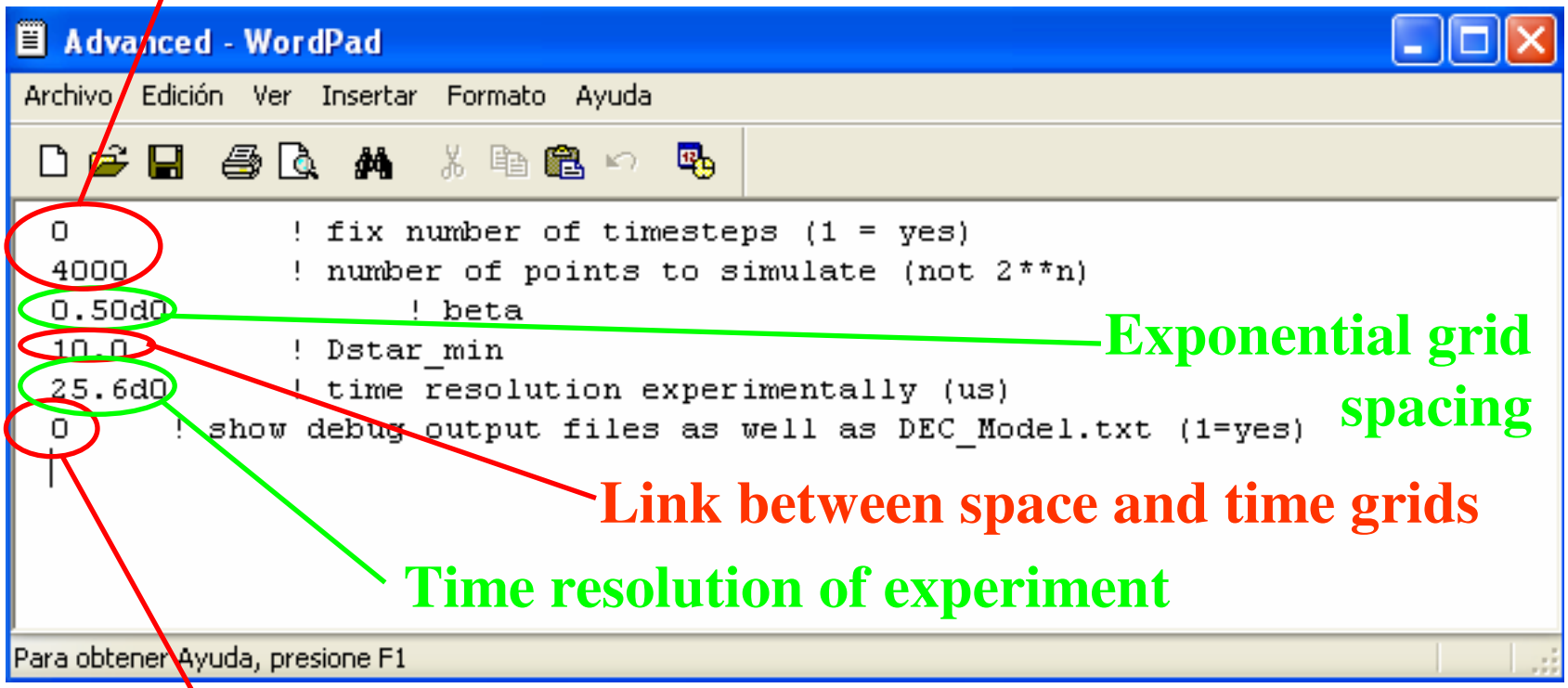
Catalytic: B = C; k_f = 10, k_b = 1

Chemical: A + B = C + D; k_f = 1000, k_b = 100

Note that the previous concentration example only had two species whereas this needs four

Advanced settings

Manually set the number of timesteps to 4000 if set to 1 here



Exponential grid spacing

Link between space and time grids

Time resolution of experiment

Set to 1 if require the output of concentration at electrode etc.

Note: Typically this input file is best left unaltered

iR effect

- Feedback between current and voltage by:

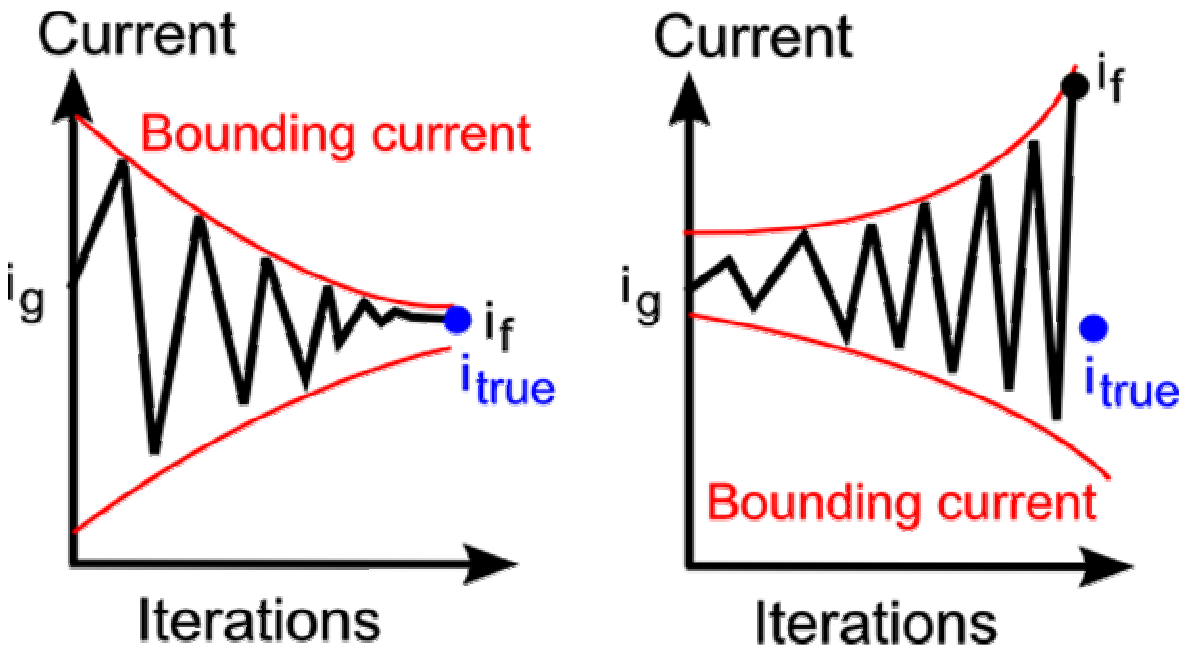
$$V = E_{app} - iR$$

$$i_F = FAk_s \left[C_B \exp\left(\frac{\alpha F(V - E^0)}{RT} \right) - C_A \exp\left(\frac{-(1-\alpha)F(V - E^0)}{RT} \right) \right]$$

- Has to be solved iteratively: (1) guess i
  (2) above equations give new V
  (3) new V gives next iteration of i when combined with surface concentrations.
  Go back to (2) with new i. Stop i doesn't change

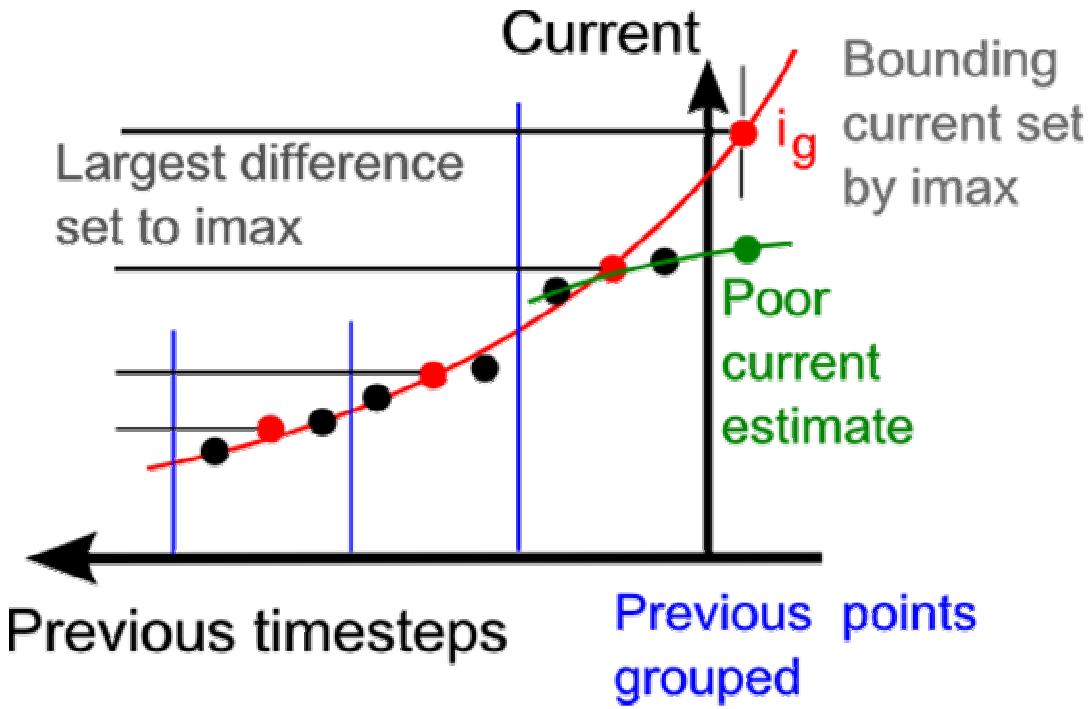
New iR method

- Difficulty making sure iteration at each timestep converges (left) and doesn't diverge (right)



New iR method

- Solved by constraining min/max bounds

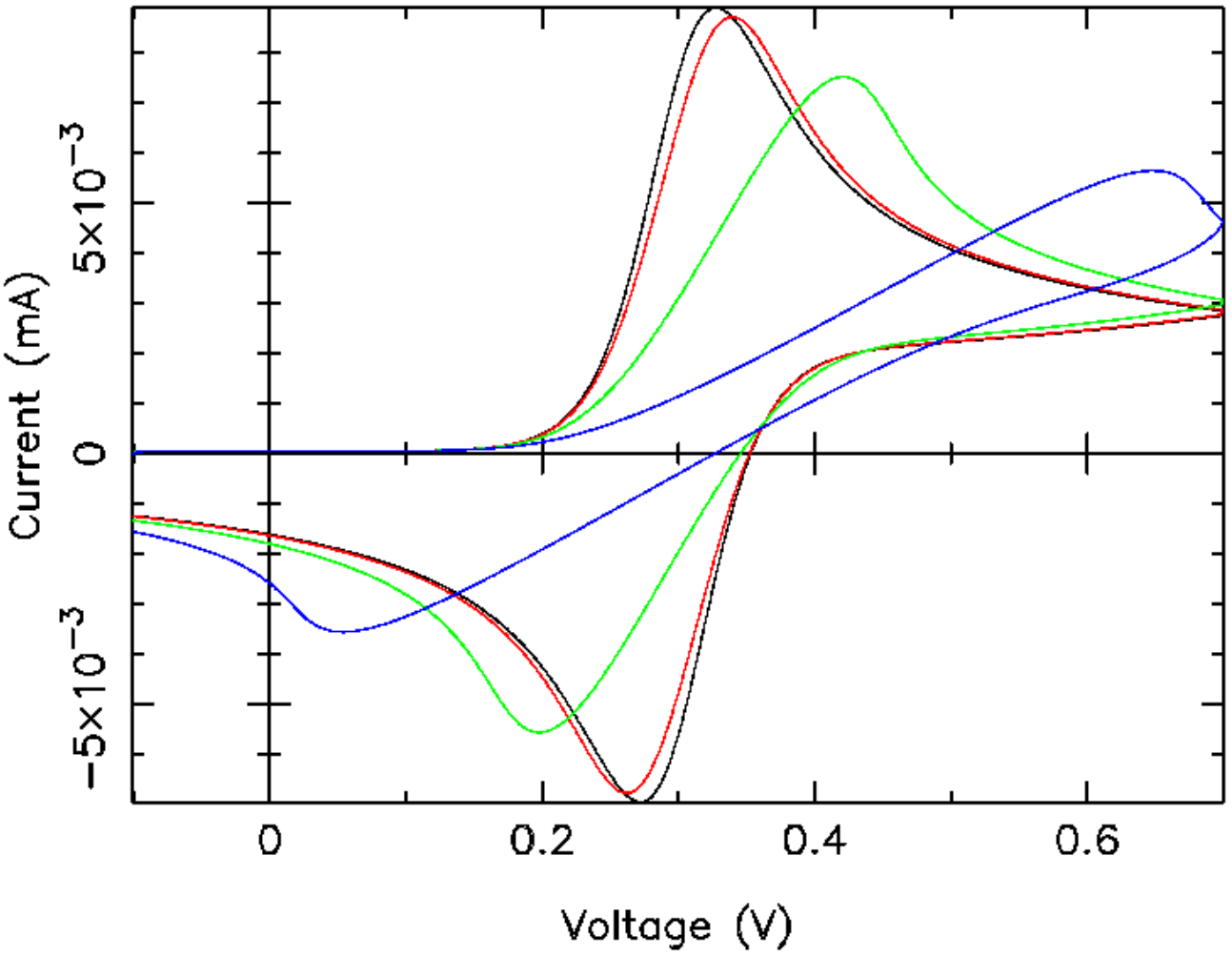


Advantages of new iR method

1. Tighter bounds on imax/min lead to less iteration required. Up to a factor of 5 quicker.
2. Insensitive to inaccurate current values for previous timesteps (due to averaging).
3. If iR were to be a problem it is expected to be easily fixed by increasing the time resolution (2^N steps in “Parameters.inp”)
4. More robust even for very high resistance (and current) values.

Affect of resistance is as expected

R =
0Ω
1kΩ
10kΩ
50Ω



Summary

- Have covered
    1. Installation
    2. Compiling and running
    3. Editing parameters for any mechanism

  of the MECSim software
- Treatment of iR effect far more robust and works as expected from theory
- Will be contactable by email at: gareth.f.kennedy@gmail.com

Thanks/References

- Alan Bond, Chongyong Lee, Stacy Konash, Barry Fleming, and Mohammad Shiddiky (Monash)
- Darrell Elton (La Trobe)
- Steve Feldberg (Brookhaven National Laboratory)

1. M. Rudolph (1995). In Israel Rubinstein (Eds), *Physical Electrochemistry*, pp. 81.
2. Press, W. B., Flannery, B. P., Teukolsky, S. A., and Vettering, W. T. (1986). *Numerical Recipes: The Art of Scientific Computing*.
3. M. Rudolph, *J. Electroanal. Chem.*, 338; 85 (1992)