

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

Filename is "Parameters.inp"

Linear Resistor

DC Ramp

Time Res
 $2^N = 2^{14}$
points

Note cursor at end of blank line

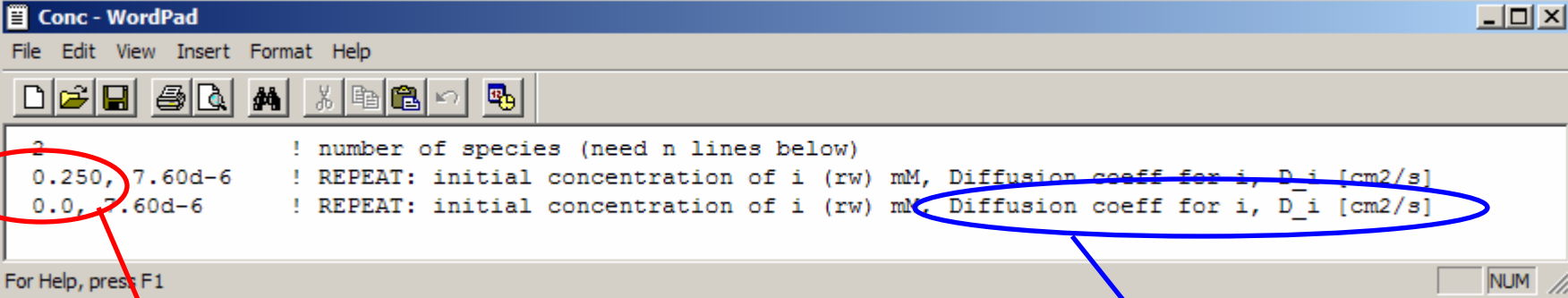
Use DC ramp as above if set to 0
Use complicated ramp if set to 1

```
Parameters - WordPad
Archivo Edición Ver Insertar Formato Ayuda

298.20          ! Temperature (K)
0.0d0          ! uncompensated resistance (ohms)
0.0            ! E_start (V)
1.0            ! E_rev (V)
1              ! number of cycles
0.10          ! scan speed (V/s)
10            ! 2**X points in time across n cycles (int)
0              ! correct for V_scan (1 = yes, 0 for no)
0              ! EC type: 0 = Butler-Volmer, 1 = Marcus-Hush theory
0              ! Pre-ecm switch: 0=stay with user entered, 1 = apply ecm (default)
1              ! use advanced voltage ramp (0 = E_start=E_end, 1 = use "Ramp.inp")

Para obtener Ayuda, presione F1
```


Concentrations

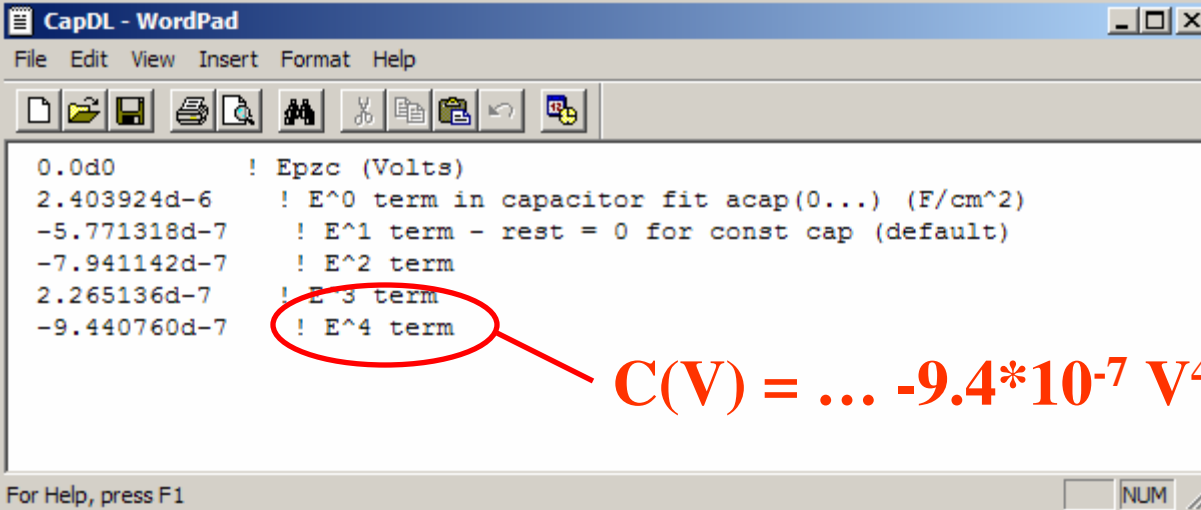


```
2          ! number of species (need n lines below)
0.250, 7.60d-6 ! REPEAT: initial concentration of i (rw) mM, Diffusion coeff for i, D_i [cm2/s]
0.0, 7.60d-6  ! REPEAT: initial concentration of i (rw) mM, Diffusion coeff for i, D_i [cm2/s]
```

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

Diffusion coefficient

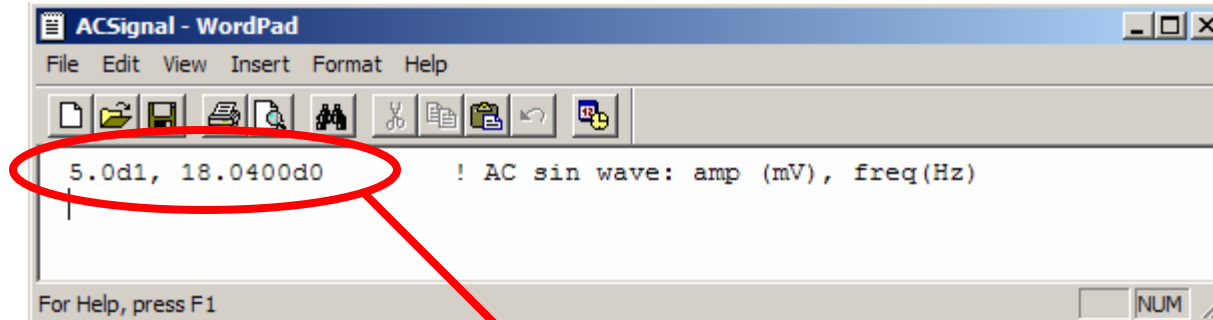
Non-linear capacitor



```
0.0d0      ! E^0 term in capacitor fit acap(0...) (F/cm^2)
2.403924d-6 ! E^1 term - rest = 0 for const cap (default)
-5.771318d-7 ! E^2 term
-7.941142d-7 ! E^3 term
2.265136d-7 ! E^4 term
-9.440760d-7
```

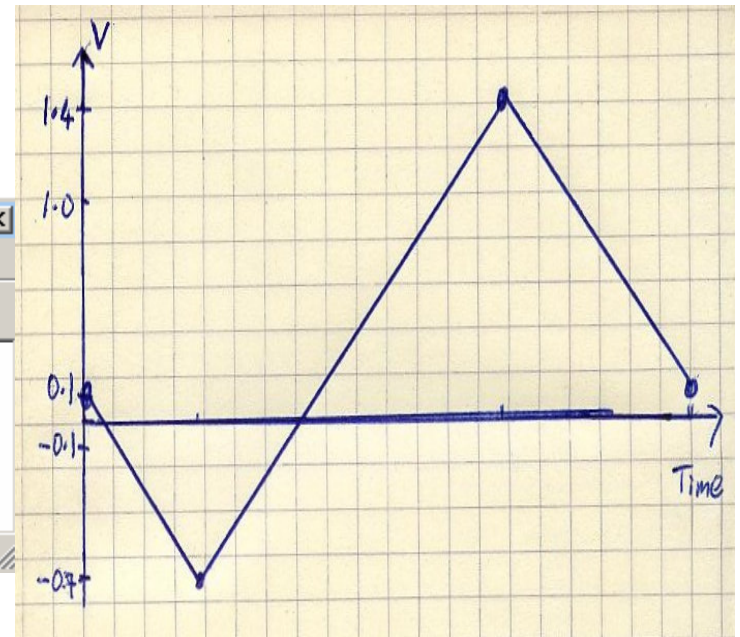
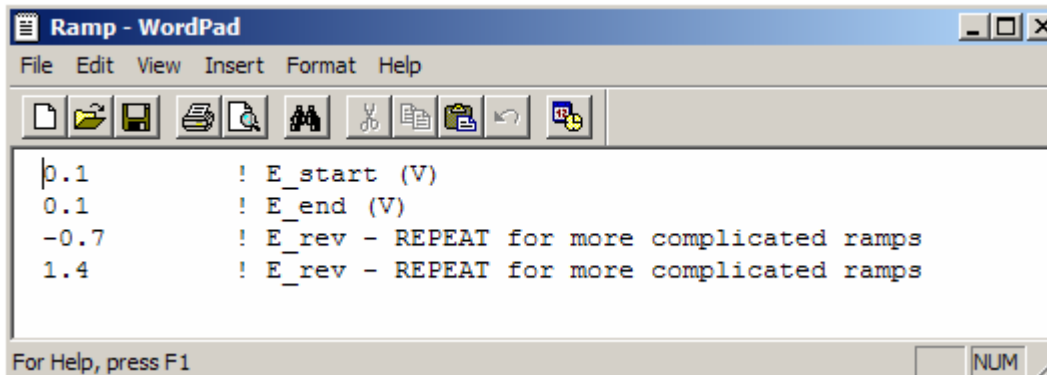
$$C(V) = \dots -9.4 \cdot 10^{-7} V^4 \text{ (F/cm}^2\text{)}$$

AC Signal added to DC ramp



Sinusoid of 50mV @ 18.04Hz

More complicated DC ramp



Electrode surface geometry

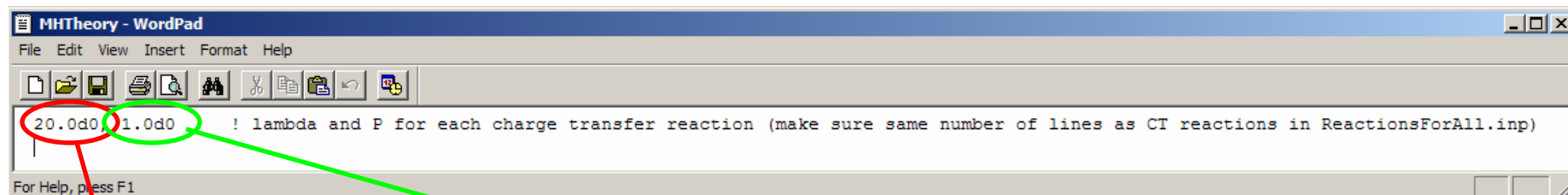
Standard
0.00349cm²

```
1      ! Geometry type (1=planar, 2=spherical, 3=cylinder (internal))
3.490d-2 ! Planar: surface area of electrode (cm^2)
5.840d9  ! Number of spheres (can be fractional)
1.0d-8   ! Radius of single sphere (cm)
0.50d0   ! Number of cylinders (can be fractional)
0.0010d0 ! Radius of single cylinder (cm)
0.370d0  ! Length of single cylinder (cm)
20.0     ! Spatial Resolution (>20)
```

**If type set to 3 then uses 1/2 of a cylinder (hemi-cylinder)
of length 0.37cm and radius 10 μ m**

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

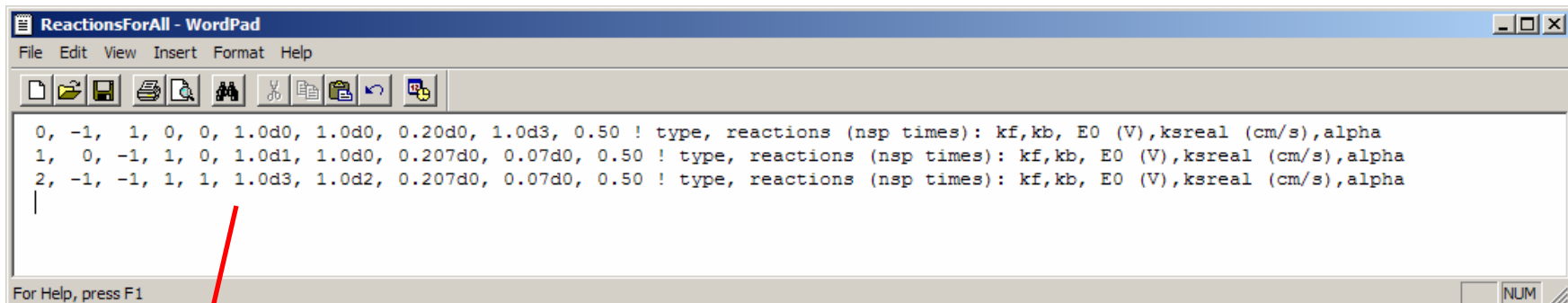
P is a constant
dependent on the type
of electrode

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:

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



```
0, -1, 1, 0, 0, 1.0d0, 1.0d0, 0.20d0, 1.0d3, 0.50 ! type, reactions (nsp times): kf, kb, E0 (V), ksreal (cm/s), alpha
1, 0, -1, 1, 0, 1.0d1, 1.0d0, 0.207d0, 0.07d0, 0.50 ! type, reactions (nsp times): kf, kb, E0 (V), ksreal (cm/s), alpha
2, -1, -1, 1, 1, 1.0d3, 1.0d2, 0.207d0, 0.07d0, 0.50 ! type, reactions (nsp times): kf, kb, E0 (V), ksreal (cm/s), alpha
```

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)

0,	-1,	1,	0,	0,	1.0d0,	1.0d0,	0.20d0,	1.0d3,	0.50	!	type,
1,	0,	-1,	1,	0,	1.0d1,	1.0d0,	0.207d0,	0.07d0,	0.50	!	typ
2,	-1,	-1,	1,	1,	1.0d3,	1.0d2,	0.207d0,	0.07d0,	0.50	!	typ

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

Forward/Backward
rates (ignored by CT)

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

Reactions input file (cont.)

CT: $A + e = B$; $E^0 = 0.2V$, $k_s = 1000 \text{ cm/s}$, $\alpha = 0.5$

```
0, -1, 1, 0, 0, 1.0d0, 1.0d0, 0.20d0, 1.0d3, 0.50 ! type,  
1, 0, -1, 1, 0, 1.0d1, 1.0d0, 0.207d0, 0.07d0, 0.50 ! typ  
2, -1, -1, 1, 1, 1.0d3, 1.0d2, 0.207d0, 0.07d0, 0.50 ! typ
```

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

```
0 ! fix number of timesteps (1 = yes)
4000 ! number of points to simulate (not 2**n)
0.50d0 ! beta
10.0 ! Dstar_min
25.6d0 ! time resolution experimentally (us)
0 ! show debug output files as well as DEC_Model.txt (1=yes)
```

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:

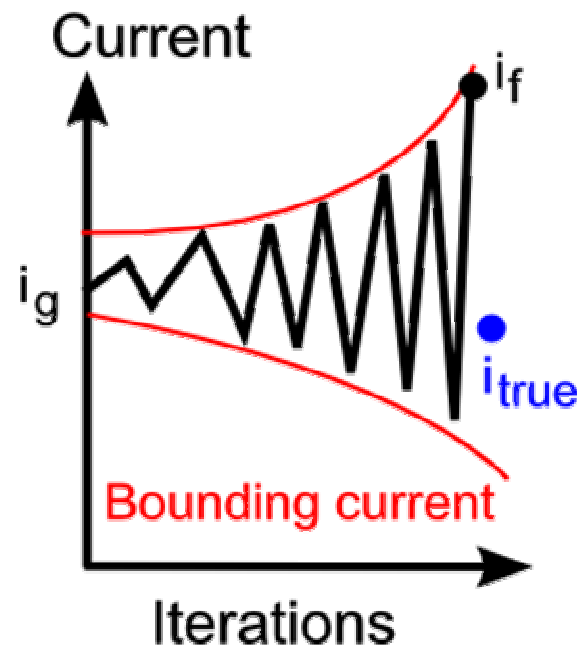
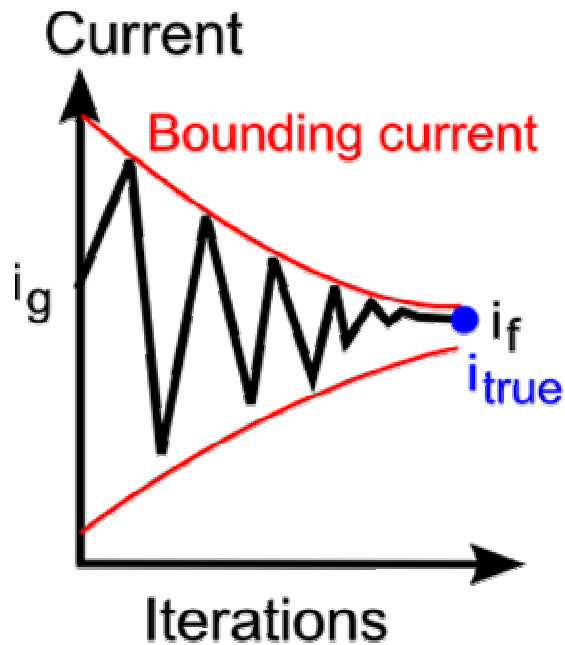
$$V = E_{app} - iR$$

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

- 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

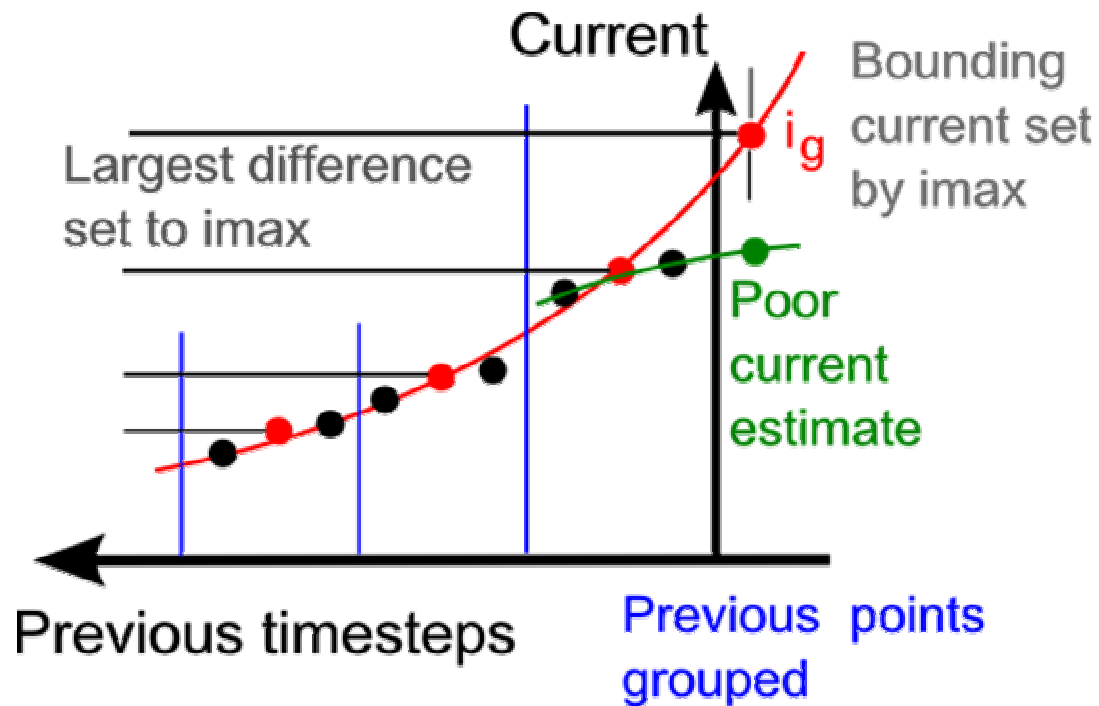
New iR method

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



New iR method

- Solved by constraining min/max bounds

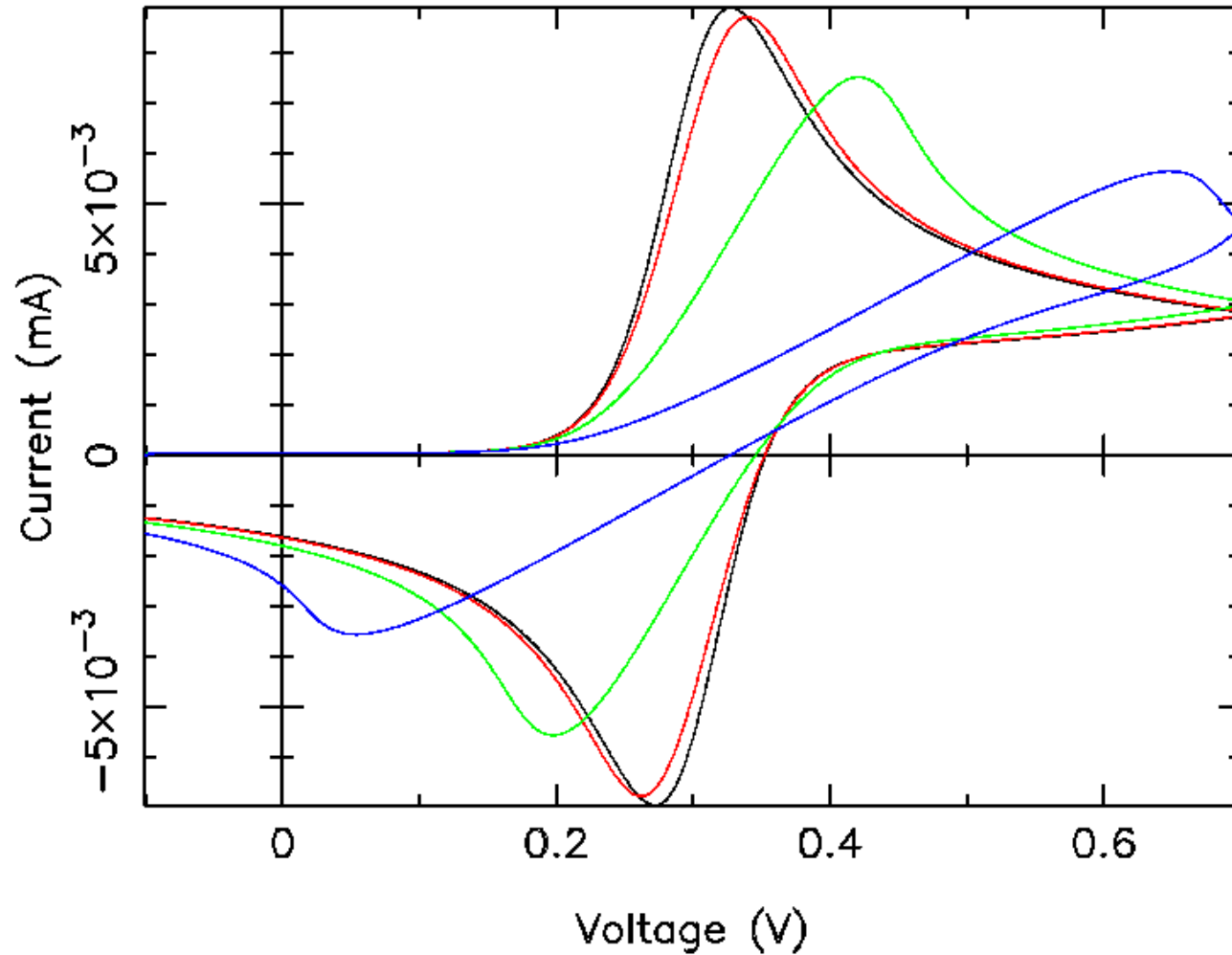


Advantages of new iR method

1. Tighter bounds on i_{\max}/i_{\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
 $1k\Omega$
 $10k\Omega$
 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 Vetterling, W. T. (1986). *Numerical Recipes: The Art of Scientific Computing*.
 3. M. Rudolph, *J. Electroanal. Chem.*, 338; 85 (1992)