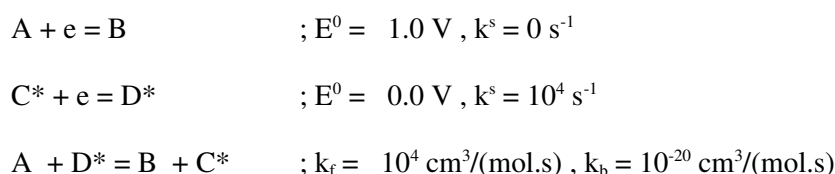


Using the MECSim input file to setup a chemical system

Gareth Kennedy, 16/11/2015

The following example will lead the reader through an example input file (called "Master.inp") which will simulate the mechanism:



where * denotes a surface confined species, the rest being in solution, and the concentrations [A] and [C*] are initially non-zero.

The Master.inp file contains all general and reaction specific parameters required to simulate any mechanism using the Monash ElectroChemical Simulation (MECSim) software package. This file is a text format file easily edited using wordpad or similar program that correctly maintains the line structure. It is assumed that this file is located in the same directory as the MECSim executable file.

We will now go through the example Master.inp file and additional comments are put where the existing comments (proceeding the "!" symbols) may not sufficiently explain the parameters.

Firstly we start with the general parameters; T, Ru, Estart (=Eend), Erev, number of cycles and the scan speed. From here on comments will follow the relevant lines in the input file.

```
298.2      ! Temperature (K)
0.0e0      ! uncompensated resistance (ohms)
0.50       ! E_start (V)
-0.50      ! E_rev (V)
1          ! number of cycles
1.0e0      ! scan speed (V/s)
12         ! 2**X points in time across n cycles (int)
```

In this case 2^{12} (=4096) time steps are requested. By setting the number of time steps to be a power of 2 greatly simplifies the calculation of the Fourier transform commonly used in the analysis.

```
0          ! correct vscan and freq for DigiPot/FFT (1 = yes, 0 for no)
```

Correction is applied to the scan rate and AC frequencies so that they exactly match with the instrumentation with a fixed sampling rate given below.

```
1          ! output type: 0=E,i,t; 1=DigiPot compatible
```

Output file type - DigiPot is the same software used to take FT experimental data in the Monash Electrochemistry group. Specifying 0 here will output a text file where for each of the 2^X points there the applied potential (V), current (A) and time (s) are outputted.

```
0          ! EC type: 0 = Butler-Volmer, 1 = Marcus theory
```

Choose the type of electron transfer theory to use. Note that this will change the meaning of the electron transfer reaction coefficients at the end of this file.

```
0          ! Pre-equilibrium switch: 0=stay with user entered, 1 = apply Pre-eqm operation
```

Apply pre-equilibration to the initial concentrations. Typically this is ok but sometimes the user may want to set up an experiment where this is inappropriate.

```
0          ! fix number of timesteps (1 = yes)
4000       ! number of points to simulate (not 2^N)
```

Use a fixed number of timesteps rather than 2^N .

```
0.10      ! beta
10.0      ! Dstar_min
0.005e0   ! max voltage step
25.6e0    ! time resolution experimentally to correct vscan/f (us)
```

These are simulation parameters that should not be changed in general. Beta is the exponential grid coefficient, a value of zero gives a uniform grid, higher values speed up calculations but may result in inaccuracies if it is too high.

```
0          ! show extra output files as well as MECSimOutput.txt
          (1=yes; 0=no)
```

Setting this to 1 will output the concentration of each species at the electrode surface as a function of time, and the final concentration profiles as a function of the distance from the electrode. However, setting this to 1 will also slow the simulation down, so it is best left as 0 unless the concentration profiles are of particular interest.

```
0          ! use advanced voltage ramp (0 = E_start=E_end, 1 = use
          advanced ramp below)
2          ! number of E_rev lines for advanced ramp (if enter 0
          then first E_rev value is the final time)
0.0        ! E_start (V)
0.0        ! E_end (V)
0.50       ! E_rev - REPEAT for more complicated ramps
-0.50      ! E_rev - REPEAT for more complicated ramps
```

These parameters are used if a non-standard dc voltage ramp is required. The above example (if the first of these lines were set to 1) would start at 0 V go up to 0.5 V, down to -0.5 V, then back up and end at 0 V. More complicated ramps can be set by increasing the number of reverse points (here it is 2, i.e. 0.5 and -0.5). Note that the number of E_rev lines must be the same as the number specified above. As with the standard dc ramp, the absolute value of the scan rate is unchanged for these "advanced" ramps. A steady voltage of single value can also be made by setting the number of reverse points to 0 and keeping a single E_rev line, which has the final time (in seconds).

```
1          ! Geometry type (1=planar, 2=spherical, 3=cylinder,
          4=RDE)
```

Select one of the four electrode types supported by MECSim: planar, spherical, cylindrical and the rotating disk electrode.

```
1.0e0      ! Planar: surface area of electrode (cm^2)
```

Set the surface area for the planar electrode.

```
1.0e0      ! Number of spheres (can be fractional)
1.0e-4     ! Radius of single sphere (cm)
```

Set the parameters for the spherical electrode. Note that a hemisphere is the same as 0.5 spheres.

```
0.50e0     ! Number of cylinders (can be fractional)
0.001e0    ! Radius of single cylinder (cm)
0.10e0     ! Length of single cylinder (cm)
```

Set the parameters for a cylindrical electrode.

```
100.0      ! Spatial Resolution (>20)
```

Technical parameter used by MECSim in non-planar electrodes. Should not be changed.

```
1.0e-1     ! RDE radius (cm)
1.0e2      ! RDE rotation speed (rad/s)
```

1.0e-5 ! RDE kinematic viscosity (cm²/s)

Set the parameters for the rotating disk electrode (RDE).

Note that $(2\pi/60)(\text{rpm}) = \text{rad/s}$, e.g. 1000 rpm is equal to 104.7198 rad/s.

1 ! number of AC sources to add (keep 1 with zero amplitude
if want DC only)

0.0e0, 18.0e0 ! AC sin wave: amp (mV), freq(Hz) (REPEAT)

Specify the number of ac sinusoids to add, and give their amplitudes and frequencies. Note that the phase is taken to be zero. The above example, where the amplitude equals zero, is equivalent to a dc ramp with NO ac sinusoids.

4 ! number of species (need n lines below)

1.0e0, 1.0e-5, 0 ! REPEAT: initial concentration of i (mol/cm³ or
mol/cm² if SC), Diffusion coeff for i, D_i [cm²/s],
surface confined (=1 for yes, else in solution)

0.0e0, 1.0e-5, 0 ! REPEAT: initial concentration of i (mol/cm³ or
mol/cm² if SC), Diffusion coeff for i, D_i [cm²/s],
surface confined (=1 for yes, else in solution)

1.0e-9, 1.0e-5, 1 ! REPEAT: initial concentration of i (mol/cm³
or mol/cm² if SC), Diffusion coeff for i, D_i [cm²/s],
surface confined (=1 for yes, else in solution)

0.0e-9, 1.0e-5, 1 ! REPEAT: initial concentration of i (mol/cm³
or mol/cm² if SC), Diffusion coeff for i, D_i [cm²/s],
surface confined (=1 for yes, else in solution)

Set the total number of chemical species and their parameters. The first column is the initial concentration in mol/cm³ for solution phase species, or mol/cm² for surface confined species. The second column is the diffusion coefficient (cm²/s), used only for solution phase species. The third column specifies if the particular species is solution (=0) or surface confined (=1). In MECSim the concentrations are referred to by the associated letter of the alphabet, i.e. the first species is referred to as A and the concentration as [A]. **Note that solution species MUST be entered first.**

The above example is equivalent to [A] = 1 mol/cm³ (equivalent to 10⁶ mM), [B] = 0 mol/cm³, [C*] = 10⁻⁹ mol/cm² and [D*] = 0 mol/cm². In MECSim the * notation is used to denote a surface confined species, and for these species the diffusion coefficient is not used by MECSim (although something still needs to be entered). The concentrations of each species will change if the pre-equilibration is set above.

Again make sure that the number of repeated lines and the set number of species is the same.

4 ! maximum a^n term for a capacitance given by $C = a_0 + a_1 V + a_2 V^2 + \dots + a_n V^n$, where $V = E_{app} - iR - E_{pzc}$. Make sure there are enough lines below to go to a^n

0.0e0 ! Epzc (Volts)

0.0e0 ! a_0 term (F/cm²)

0.0e0 ! a_1 term

0.0e0 ! a_2 term

0.0e0 ! a_3 term

0.0e0 ! a_4 term

These specify the background capacitance. The first term gives the maximum order of the polynomial used to describe the background. The polynomial is given by $C(V) = a_0 + a_1 V + a_2 V^2 + a_3 V^3 + a_4 V^4$ where the a_i terms are what is specified above and V is the voltage which incorporates any IR drop. The simplest case is setting the a_0 term only, i.e. $C = a_0 = C_{dl}$, which does not depend on the potential. Make sure that the number of lines is the same as the requested order of the polynomial.

```

0, -1, 1, 0, 0, 1.0e0, 1.0e0, 1.0e0, 0.0e4, 0.50e0      ! type,
    reactions (nsp times): kf, kb, E0 (V), ksreal (cm/s), alpha
    for BV or lambda* for MH (1eV) (REPEAT FOR EACH REACTION)
0, 0, 0, -1, 1, 1.0e0, 1.0e0, 0.0e0, 1.0e4, 0.50e0      ! type,
    reactions (nsp times): kf, kb, E0 (V), ksreal (cm/s), alpha
    for BV or lambda* for MH (1eV) (REPEAT FOR EACH REACTION)
2, -1, 1, 1, -1, 1.0e-4, 1.0e-20, 0.20e0, 1.0e0, 0.50e0 ! type,
    reactions (nsp times): kf, kb, E0 (V), ksreal (cm/s), alpha
    for BV or lambda* for MH (1eV) (REPEAT FOR EACH REACTION)

```

The setting up of the reactions will be treated in more detail below, but a quick description of this mechanism is made here. Basically each line is a reaction and the first column gives the type of reaction; 0=charge transfer ($A + e = B$), 1=first order chemical ($A = B$), 2=second order chemical ($A + B = C + D$). The next n columns refer to each chemical species and describe their participation in each reaction, where n is set by the total number of species, 4 in this example. The participation is specified by a -1 if it appears on the left hand side of a given reaction, and 1 if it is on the right hand side. For the case of multiple electron transfers of the form $A + ne = B$ then it would be written as -1 in the "A" column and 2 in the "B" column. **MECSim always requires input of charge transfer reactions in reduction form.** The next 2 columns are k_f and k_b used if the reaction is a chemical reaction. The final 3 columns are E^0 , k_s and α (or λ in eV if Marcus-Hush theory is requested). The reaction lines translate as:

1. $A + e = B$ with $E^0 = 1 \text{ V}$, $k_s = 0 \text{ s}^{-1}$ and $\alpha = 0.5$
2. $C^* + e = D^*$ with $E^0 = 0 \text{ V}$, $k_s = 10^4 \text{ s}^{-1}$ and $\alpha = 0.5$
3. $A + D^* = B + C^*$ with $k_f = 10^{-4} \text{ cm}^3/(\text{mol.s})$ and $k_b = 10^{-20} \text{ cm}^3/(\text{mol.s})$

Note that the units for k_f and k_b depend on the type of chemical reaction.

There are two rules for reactions that involve surface confined species. Firstly, the same number of surface species must exist on the left hand side as well as the right hand side, so $A = B^*$ is not permitted. Secondly, the solution charge transfer reactions must be entered before the surface confined charge transfer reactions.

Adsorption can be modelled by having a pre-existing species on the electrode which interacts with something in solution to become something that is active on the surface. E.g. $A + B^* = C^*$, followed by $C^* + e = D^*$. But a warning must be given that it is easy to simulate a mechanism that may not be physically realistic.

Units warning: 2nd order reaction rates are in mol and cm units to facilitate reactions involving both surface confined and solution phase species. For example the k_{fb} in $A + D^* = B + C^*$ (3 above) is in units of $\text{cm}^3/(\text{mol.s})$, and the k_{fb} in $A + B = C + D$ would also be in units of $\text{cm}^3/(\text{mol.s})$. When converting these reaction rates into use with DigiSim or DigiElch (which are in SI units) then the second order chemical reaction rates in $\text{cm}^3/(\text{mol.s})$ for MECSim k_f and k_b need to be multiplied by 10^3 , to get into $1/(\text{Molar.s})$.

Another complication that comes with entering a large and interdependent reaction network is that some equilibrium constants are not independent on those previously set. These reactions are referred to as Thermodynamically Superfluous Reactions (TSRs). MECSim automatically adjusts equilibrium constants based on the reactions specified on the lines above in the Master.inp file. When a TSR is detected MECSim will output a warning to screen, adjust the K_{eq} value for the reaction, and calculate k_b for that reaction taking the input k_f value as being true. This can lead to issues for large reaction networks, in that what the user thinks they have entered (k_f , k_b for all reactions) is not exactly what has been run by MECSim. Always check the output to screen which will give all of the k_f and k_b values for all reactions, corrected for any TSRs.

Note that a blank line must be left at the "Master.inp" file.

More on entering reactions

Points to remember:

- Enter one line per reaction
- Ensure you have the correct number of columns after the reaction type. This should be the same as the total number of chemical species.
- Make sure there is a blank line at the end of the file

Below is shown another example of entering the following mechanism;

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

**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**

**-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)**

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 !	tyr
2, -1, -1, 1, 1,	1.0d3, 1.0d2,	0.207d0, 0.07d0, 0.50 !	tyr

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

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

Cautions and known limitations

Rotating disk electrodes

For a rotating disk electrode under certain conditions the current will get to a steady-state value given by the Levich equation. The Levich equation is

$$I_{ss} = 0.620 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C$$

where n is the number of electrons transferred, A is the electrode area (cm^2), D is the diffusion coefficient (cm^2/s) of solution species with concentration C (mol/cm^3), ω is the angular rotation (rad/s) and ν is the kinematic viscosity (cm^2/s). Typically MECSim gives a steady state current that is within 1% of the theoretical Levich current. This slight difference is also seen in comparisons with DigiElch and is due to differences in how the different models set the kinematic viscosity and diffusion coefficients as a function of distance from the electrode.

Entering sequential charge transfer reactions

All reactions must be entered into MECSim using the reduction format, i.e. $A + e = B$; $B + e = C$. Reactions entered as $C + e = B$; $B + e = A$ are not always recognised by the MECSim software, so results may be unexpected.

This is an example of a **valid** entered reaction:

```
0, -1, 1, 0, 0e0, 0e0, 0.00, 1e6, 0.50 ! type, reactions (nsp
times): kf, kb, E0 (V), ksreal (cm/s), alpha for BV or lambda* for MH
(1eV) (REPEAT FOR EACH REACTION)
0, 0, -1, 1, 0e0, 0e0, 0.20, 1e6, 0.50 ! type, reactions (nsp
times): kf, kb, E0 (V), ksreal (cm/s), alpha for BV or lambda* for MH
(1eV) (REPEAT FOR EACH REACTION)
```

This is an **invalid** entered reaction:

```
0, 1, -1, 0, 0e0, 0e0, 0.20, 1e6, 0.50 ! type, reactions (nsp
times): kf, kb, E0 (V), ksreal (cm/s), alpha for BV or lambda* for MH
(1eV) (REPEAT FOR EACH REACTION)
0, 0, 1, -1, 0e0, 0e0, 0.00, 1e6, 0.50 ! type, reactions (nsp
times): kf, kb, E0 (V), ksreal (cm/s), alpha for BV or lambda* for MH
(1eV) (REPEAT FOR EACH REACTION)
```

Rate constants

Issue if rate constants exceed 10^{10} , which is needlessly large for physical systems.