

CVFit Instructions

(author: M. Hazoglou)

Before running the program, you need to change the extension on the downloaded file from `ex_` to `exe`. Then double click on the file to start. An MS-DOS window should open up. Follow the instructions below. Note that all input files must be in the same directory as the program. Also, all output files are written to this same directory.

1. Introduction. This program is designed to fit both the forward and reverse half waves of a cyclic voltammetry (CV) scan, in the presence of 0, 1, or 2 reversible, surface-immobilized redox species (referred to as "tags" or "peaks"). The program calculates the area of the peaks, and estimates the experimental baselines by using the following equations (I_B : baseline current; I_T : current from redox tags; I_{EX} : total experimental current):

$$I_B = a_1 + a_2V + a_3(\exp\left(\frac{V^{a_4}}{a_5}\right) - 1) \quad \text{eqn. 1}$$

$$I_T = a_{6,T} \exp\left(a_{8,T}(V - a_{7,T})\right) / [1 + \exp\left(a_{8,T}(V - a_{7,T})\right)]^2 \quad \text{eqn. 2}$$

$$I_{EX} = I_B + I_{T,F2} + I_{T,F1} \quad \text{eqn. 3}$$

The subscripts " EX ", " B ", " $T, F1$ " and " $T, F2$ " denote the total experimental current, background current, the first tag current and the second tag current, respectively. V is the potential of the electrode and the various a 's are fitting constants. A full set of eight a 's is used for the forward wave. The reverse wave uses just seven a 's because a_8 on the reverse wave is constrained by the requirement that the forward and reverse peak areas be equal. In the program input and output files (see below), parameters referring to the forward wave have an appended "f", those referring to the reverse wave have an appended "r". a_1 and a_2 represent linear portion (called intercept and slope, respectively) of the baseline. a_3 through a_5 (called prefactor, power, and denominator, respectively) are used to model the typical upturn in baseline current as V increases due to onset of background charge transfer processes. a_6 is related to the area of a surface redox peak, and is called tagprefc. a_7 represents the potential at which the maximum peak current is observed, and is referred to as tag E0 in the parameter file. a_8 describes the width of the peak and is referred to as tagwidth.

2. Fitting a Data Set.

Fitting foremost requires good initial guesses. Depending on how many redox peaks are present the program might require optimization of up to 20 parameters, and this problem is difficult enough to cause it to diverge if the initial guesses are not sufficiently good. In one approach, a portion of the CV trace outside the peaks can be used to first derive the intercept and slope parameters for the forward and reverse traces. These can then be used as inputs in a second round of fitting in which the other parameters are derived. As described below, during a particular fitting round each parameter can be allowed to vary or be constrained to remain at the input value, as desired. It takes some practice to get a feel for how to best approach fitting of a particular type of dataset.

The program is started by double-clicking on it. All input and output files are read from or written out to the same directory in which CVfit is. File names are restricted to less than 40 characters. The present version of the program assumes the CV starts by scanning in the positive direction.

1). The user is first asked to input the name of the CV file, which is a text file assumed to have three columns: 1). potential in volts, 2). current in amperes, and 3) the integrated charge. This format is for compatibility with the potentiostat software we use. Although 3 columns are required for the file to be read in correctly, the last column (charge) is not used for any calculations and is read in as "dummy" data. The format of our CV data files looks like (other column formats may also work):

```
0.000 1.801e-7      9.005e-12
0.001 1.837e-6      1.009e-10
0.002 2.936e-6      2.477e-10
0.003 3.443e-6      4.198e-10
0.004 3.708e-6      6.052e-10
0.005 3.940e-6      8.023e-10
0.006 4.007e-6      1.003e-9
0.007 4.072e-6      1.206e-9
etc.
```

2). If the CV data contains negative potentials the program will ask to shift (translate) the potentials so as to make all potential values positive. Reply "y" for yes as the program can only work with positive potentials. The value of the shift in potential applied by the program will be saved in the output parameters file "fitdat____.txt" as the "V shift", and can be later subtracted if so desired. The shift does not affect the peak areas calculated.

3) Next, the user is asked to enter the name of the input parameter file. This file must have the format (including exact # spaces) as shown below up through "tag2 E0 r" (any additional text is ignored). The input file can be edited, for example, with Wordpad. The first column identifies the parameter (the parameters must be in this order), the second column provides the parameter value in double precision (format must be exactly as shown, including the "D" which indicates double precision), the third column is 0 if the parameter is free to vary so that it can be optimized and 1 if it is to be kept fixed. In the fourth column, place a 1 if the parameter is used by the model, and 0 if it is not. For example, the below file is designed to only fit on the linear parts of the baseline. This is done by keeping the intercept and slope of the forward and reverse traces "free" in the 3rd column, and fixing all other parameters. In the 4th column, only the intercept and slope parameters are indicated as used by the model. In the second column, the prefactors for the tags as well as the nonlinear part of the baseline are set to zero so that these terms do not contribute to the total current I_{EX} . The fifth column must be present but is only relevant if a 2 was placed in the 3rd column. The 2 indicates, for a reverse trace parameter only, that it is to be made proportional to the corresponding parameter on the forward trace, with the proportionality factor given by the double precision value in the 5th column.

```
interceptf  -0.4410046995845555D-05      0      1      0.0000000000000000D+00
slopef      -0.4533052401891081D-05      0      1      0.0000000000000000D+00
prefacf     -0.0000000000000000D-03      1      0      0.0000000000000000D+00
powerf      0.2678868590952838D+00      1      0      0.0000000000000000D+00
```

denomf	0.3105918919347357D-01	1	0	0.0000000000000000D+00
tag1prefcf	-0.0000000000000000D-03	1	0	0.0000000000000000D+00
tag1 E0 f	0.3637803215578048D+00	1	0	0.0000000000000000D+00
tag1widthf	0.3077595297389197D+02	1	0	0.0000000000000000D+00
tag2prefcf	-0.0000000000000000D-03	1	0	0.0000000000000000D+00
tag2 E0 f	0.5221087253869634D+00	1	0	0.0000000000000000D+00
tag2widthf	0.2765917304818829D+02	1	0	0.0000000000000000D+00
interceptr	0.5330422790584973D-05	0	1	0.0000000000000000D+00
sloper	0.2019014142668317D-05	0	1	0.0000000000000000D+00
prefacr	-0.0000000000000000D-04	1	0	0.1000000000000000D+01
powerr	0.8570692063750290D+00	1	0	0.1000000000000000D+01
denomr	0.3000130310152646D-01	1	0	0.1000000000000000D+01
tag1prefcr	-0.0000000000000000D-02	1	0	0.0000000000000000D+00
tag1 E0 r	0.3697137646288154D+00	1	0	0.0000000000000000D+00
tag2prefcf	-0.0000000000000000D+00	1	0	0.0000000000000000D+00
tag2 E0 r	0.5482510092047562D+00	1	0	0.0000000000000000D+00

4). Next, the user has to input the lower limits and the upper limits of the forward and backwards scans to designate the portions on which the fitting is to be performed. For the above example, one wants to select the region of the data that is reasonably linear in order to estimate the intercept and slope parameters. Fig. 1 shows an example CV trace. Reasonable limits for the forward trace could be 0.05 V to 0.15V, for the reverse trace they could be 0.0 V to 0.15V. The limits should be chosen so as to avoid the initial rise in current at the beginning of the forward and reverse traces, which the program is not designed to fit.

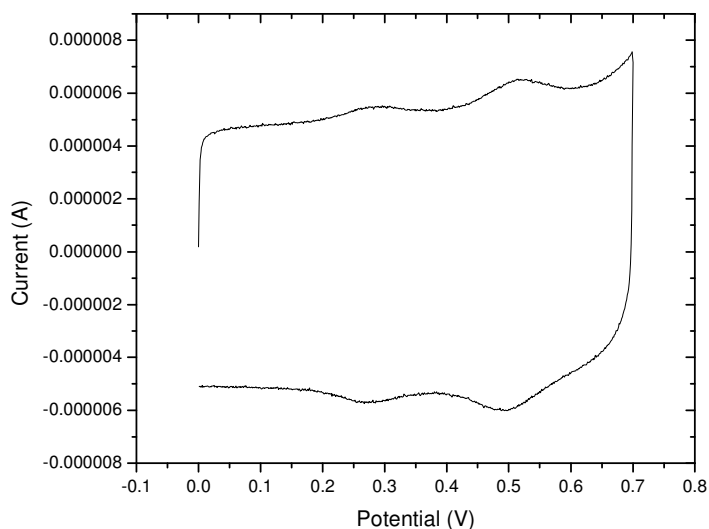


Figure 1.

5) Next, the number of tags is entered, which for the case of fitting just the linear baseline portion is 0.

6) The temperature the experiment was conducted is entered next in degrees Kelvin.

7) The number of fitting parameters is displayed (which should be 4 for the example). The user then presses enter to start fitting.

8) When done with the fitting, the program will display the "optfnc" value. In our experience, a value that is on the order of 1×10^{-6} or less is a good fit. This, however, depends on the noisiness of the data, so other values would apply to other data sets. Press enter to exit the program.

9) The program will have written two new files called fitdat____.txt: this file contains values of the fit parameters and additional information, as shown below:

```

interceptf  -0.4579258857751008D-05      0      1      0.0000000000000000D+00
slopef      -0.1858102464338593D-05      0      1      0.0000000000000000D+00
prefacf     0.0000000000000000D+00      1      0      0.0000000000000000D+00
powerf      0.2678868590952838D+00      1      0      0.0000000000000000D+00
denomf      0.3105918919347357D-01      1      0      0.0000000000000000D+00
tag1prefcf  0.0000000000000000D+00      1      0      0.0000000000000000D+00
tag1 E0 f   0.3637803215578048D+00      1      0      0.0000000000000000D+00
tag1widthf  0.3077595297389197D+02      1      0      0.0000000000000000D+00
tag2prefcf  0.0000000000000000D+00      1      0      0.0000000000000000D+00
tag2 E0 f   0.5221087253869634D+00      1      0      0.0000000000000000D+00
tag2widthf  0.2765917304818829D+02      1      0      0.0000000000000000D+00
interceptr  0.5085442426920689D-05      0      1      0.0000000000000000D+00
sloper      0.6235419368577152D-06      0      1      0.0000000000000000D+00
prefacr     0.0000000000000000D+00      1      0      0.0000000000000000D+00
powerr      0.8570692063750290D+00      1      0      0.0000000000000000D+00
denomr      0.3000130310152646D-01      1      0      0.0000000000000000D+00
tag1prefcr  0.0000000000000000D+00      1      0      0.0000000000000000D+00
tag1 E0 r   0.3697137646288154D+00      1      0      0.0000000000000000D+00
tag2prefcr  0.0000000000000000D+00      1      0      0.0000000000000000D+00
tag2 E0 r   0.5482510092047562D+00      1      0      0.0000000000000000D+00
nF/RT      0.3933730154289113D+02
v start f   0.5000000000000000D-01
v end f     0.1490000000000000D+00
v start r   0.1000000000000000D-02
v end r     0.1490000000000000D+00
optfnc      0.3478986445668222D-06
V shift     0.0000000000000000D+00
tag1 area   0.000000E+00
tag2 area   0.000000E+00

```

Optfnc is the optimized error value. Also, the output fitdat file shows the limits on potential used, and the areas of tag peaks (if any).

The other file output by the program is fits____.txt which contains the experimental as well as calculated curves. In the present case, the first column is the experimental potential, the second is the experimental current, the third is the calculated current from the fit (Fig. 2).

```

0.5000000000000000D-01      -0.4648000000000001D-05      -0.4672163980967938D-05
0.5100000000000000D-01      -0.4661000000000000D-05      -0.4674022083432277D-05
0.5200000000000000D-01      -0.4719000000000000D-05      -0.4675880185896616D-05
0.5300000000000000D-01      -0.4694000000000000D-05      -0.4677738288360954D-05
0.5400000000000000D-01      -0.4694000000000000D-05      -0.4679596390825293D-05
0.5500000000000000D-01      -0.4670000000000000D-05      -0.4681454493289631D-05

```

etc.

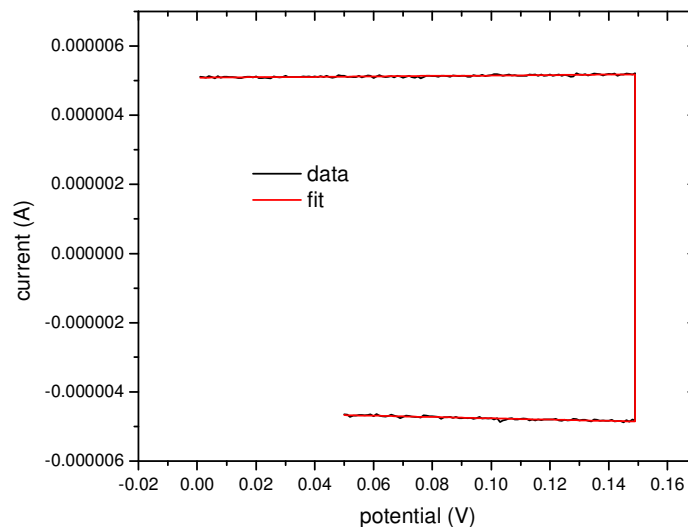


Figure 2.

As seen in Figure 2, the program outputs the fits with the forward scan always on the bottom (i.e. corresponding to negative current). This is the form of the CV the program works with. It is important to keep this in mind when choosing initial guesses, as it determines the signs of the various prefactor quantities. If the prefactor guesses are assigned wrong signs, the program will likely not be able to converge.

NOTE: In writing the two output files, the program will automatically overwrite any pre-existing files of the same name.

10). Next, one wants to fit the entire CV curve. This is also best done in stages, keeping the number of parameters fit at each stage as small as possible, and using as good as possible initial guesses. For this next step, the fitdat file from step 9 can be edited (e.g. using Wordpad) to look as shown below:

```

interceptf  -0.4579258857751008D-05    1    1    0.0000000000000000D+00
slopef      -0.1858102464338593D-05    0    1    0.0000000000000000D+00
prefacf     -0.1000000000000000D-18    0    1    0.0000000000000000D+00
powerf      0.1000000000000000D+00      0    1    0.0000000000000000D+00
denomf      0.5000000000000000D-01    0    1    0.0000000000000000D+00
tag1prefcf  -0.1000000000000000D-05    0    1    0.0000000000000000D+00
tag1 E0 f   0.2800000000000000D+00      1    1    0.0000000000000000D+00
tag1widthf  0.3933730154289113D+02      0    1    0.0000000000000000D+00
tag2prefcf  -0.1000000000000000D-05    0    1    0.0000000000000000D+00
tag2 E0 f   0.5100000000000000D+00      1    1    0.0000000000000000D+00
tag2widthf  0.3933730154289113D+02      0    1    0.0000000000000000D+00
interceptr  0.5085442426920689D-05    1    1    0.0000000000000000D+00
sloper      0.6235419368577152D-06    0    1    0.0000000000000000D+00
prefacr     -0.1000000000000000D-18    2    1    0.1000000000000000D+01
powerr      0.1000000000000000D+00    2    1    0.1000000000000000D+01
denomr      0.5000000000000000D-01    2    1    0.1000000000000000D+01
tag1prefcr  0.1000000000000000D-05    0    1    0.0000000000000000D+00
tag1 E0 r   0.2700000000000000D+00      1    1    0.0000000000000000D+00

```

```

tag2prefcf      0.1000000000000000D-05      0      1      0.0000000000000000D+00
tag2 E0 r      0.5000000000000000D+00      1      1      0.0000000000000000D+00
nF/RT          0.3933730154289113D+02
v start f      0.5000000000000000D-01
v end f        0.1490000000000000D+00
v start r      0.1000000000000000D-02
v end r        0.1490000000000000D+00
optfnc         0.3478986445668222D-06
V shift        0.0000000000000000D+00
tag1 area      0.000000E+00
tag2 area      0.000000E+00

```

Note that all parameters are now being used (4th column). In the 3rd column, the intercepts of the forward and reverse half waves have been fixed, as from experience these are pretty well optimized from the prior fit of the linear baseline portion. Also, all peak potentials were fixed, as these can be estimated quite accurately from the experimental CV (Figure 1). The curved part of the baseline on the reverse trace was assumed to be the same as that on the forward trace, as indicated by the "2"s in the 3rd column and the corresponding proportionality factors of 1 in the 5th column. This still leaves 11 parameters to be fit. From these, the initial guesses for the two slopes are as determined from the linear baseline fit. The initial guesses for the peak width parameters of the two tags are estimated from the theoretically expected nF/RT value (n: number of electrons involved in oxidation/reduction of the peak – assumed to be 1; F: Faraday's constant). If n is other than 1, the nF/RT quantity should be appropriately adjusted. Also, order of magnitude estimates have been entered as initial guesses for the four tag prefactors. These can be derived from a back-of-the-envelope estimate of the experimental peak areas and the nF/RT estimate for tagwidth using the formula (derived from eqn 2)

$$\text{Peak area} = \text{tagprefc}/\text{tagwidth} = a_6/a_8 \quad \text{eqn 4.}$$

$$\text{tagprefc} = (\text{peak area}) * nF/RT$$

It is important to note the signs on the tagprefc parameters – these are negative for the forward scan, positive for the reverse scan. If the signs are entered incorrectly, the program will likely not converge.

The most difficult parameters to provide good initial guesses for are the prefac, power and denom of the curved portion of the baseline (a_3 , a_4 , and a_5 in eqn 1). The file above has some typical values as initial guesses.

11). The CV fitting is now repeated as before, except that the above file is used as the input parameter file, and the potential ranges for the fit now span most of the CV range – e.g. 0.05 to 0.68 V for the forward and 0 to 0.65 V for the reverse half waves. The main caution in choosing these ranges is to avoid the transient behavior observed at the extremes. Also, when prompted, the user must now enter "2" as the number of tags being used. The results of the fit are shown below (fitdat file),

```

interceptf     -0.4579258857751008D-05      1      1      0.0000000000000000D+00
slopef         -0.9396798099829628D-06      0      1      0.0000000000000000D+00
prefacf        -0.1701191940073260D-18      0      1      0.0000000000000000D+00
powerf         0.2329477534020960D+00      0      1      0.0000000000000000D+00
denomf         0.3055414497085411D-01      0      1      0.0000000000000000D+00
tag1prefcf     -0.2345626070388891D-05      0      1      0.0000000000000000D+00

```

```

tag1 E0 f      0.2800000000000000D+00      1      1      0.0000000000000000D+00
tag1widthf    0.2205991361112690D+02      0      1      0.0000000000000000D+00
tag2prefcf   -0.4585383402771432D-05      0      1      0.0000000000000000D+00
tag2 E0 f     0.5100000000000000D+00      1      1      0.0000000000000000D+00
tag2widthf    0.2687933605581954D+02      0      1      0.0000000000000000D+00
interceptr    0.5085442426920689D-05      1      1      0.0000000000000000D+00
sloper       -0.1414647491037366D-06      0      1      0.0000000000000000D+00
prefacr      -0.1701191940073260D-18      2      1      0.1000000000000000D+01
powerr       0.2329477534020960D+00      2      1      0.1000000000000000D+01
denomr       0.3055414497085411D-01      2      1      0.1000000000000000D+01
tag1prefcr   0.2454373013688446D-05      0      1      0.0000000000000000D+00
tag1 E0 r     0.2700000000000000D+00      1      1      0.0000000000000000D+00
tag2prefcf   0.4513872781467255D-05      0      1      0.0000000000000000D+00
tag2 E0 r     0.5000000000000000D+00      1      1      0.0000000000000000D+00
nF/RT        0.3933730154289113D+02
v start f     0.5000000000000000D-01
v end f       0.6790000000000000D+00
v start r     0.1000000000000000D-02
v end r       0.6490000000000000D+00
optfnc       0.1447567838253108D-05
V shift       0.0000000000000000D+00
tag1 area     0.106330E-06
tag2 area     0.170591E-06

```

The output "fits" file will now have 6 columns. The first column is the potential, the second is the experimentally measured current, the third is the fitted baseline current (I_B), the fourth is the fitted tag 1 peak ($I_{T,1}$), the fifth is the fitted tag 2 peak ($I_{T,2}$), and the sixth is the total fitted current (I_{EX}). These are shown in the below plot.

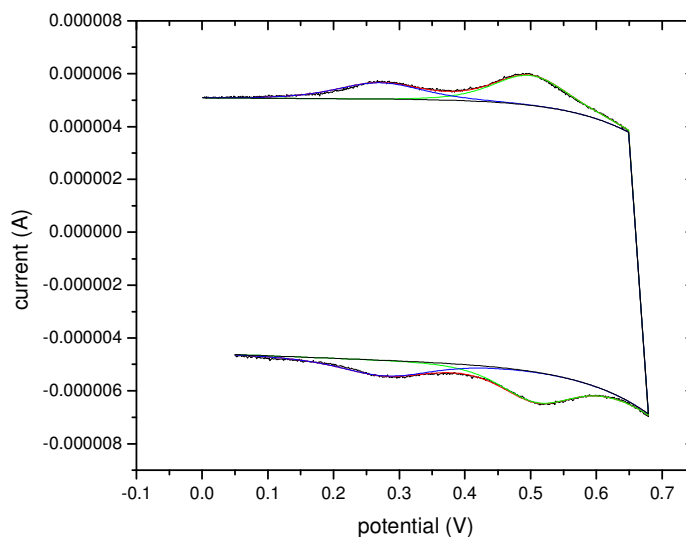


Figure 3.

12). Lastly, the fit is optimized. The input file is edited to look as follows, allowing all 20 parameters to be varied, but otherwise keeping the values from the preceding step:

interceptf	-0.4579258857751008D-05	0	1	0.0000000000000000D+00
slopef	-0.9396798099829628D-06	0	1	0.0000000000000000D+00
prefacf	-0.1701191940073260D-18	0	1	0.0000000000000000D+00
powerf	0.2329477534020960D+00	0	1	0.0000000000000000D+00
denomf	0.3055414497085411D-01	0	1	0.0000000000000000D+00
tag1prefcf	-0.2345626070388891D-05	0	1	0.0000000000000000D+00
tag1 E0 f	0.2800000000000000D+00	0	1	0.0000000000000000D+00
tag1widthf	0.2205991361112690D+02	0	1	0.0000000000000000D+00
tag2prefcf	-0.4585383402771432D-05	0	1	0.0000000000000000D+00
tag2 E0 f	0.5100000000000000D+00	0	1	0.0000000000000000D+00
tag2widthf	0.2687933605581954D+02	0	1	0.0000000000000000D+00
interceptr	0.5085442426920689D-05	0	1	0.0000000000000000D+00
sloper	-0.1414647491037366D-06	0	1	0.0000000000000000D+00
prefacr	-0.1701191940073260D-18	0	1	0.1000000000000000D+01
powerr	0.2329477534020960D+00	0	1	0.1000000000000000D+01
denomr	0.3055414497085411D-01	0	1	0.1000000000000000D+01
tag1prefcr	0.2454373013688446D-05	0	1	0.0000000000000000D+00
tag1 E0 r	0.2700000000000000D+00	0	1	0.0000000000000000D+00
tag2prefcr	0.4513872781467255D-05	0	1	0.0000000000000000D+00
tag2 E0 r	0.5000000000000000D+00	0	1	0.0000000000000000D+00
nF/RT	0.3933730154289113D+02			
v start f	0.5000000000000000D-01			
v end f	0.6790000000000001D+00			
v start r	0.1000000000000000D-02			
v end r	0.6490000000000000D+00			
optfnc	0.1447567838253108D-05			
V shift	0.0000000000000000D+00			
tag1 area	0.106330E-06			
tag2 area	0.170591E-06			

The fit is rerun with the same potential limits as before, and again indicating that 2 tags (peaks) are being used. The optimized results are shown below:

interceptf	-0.4632565522417892D-05	0	1	0.0000000000000000D+00
slopef	-0.9152279214138414D-06	0	1	0.0000000000000000D+00
prefacf	-0.1693406064100367D-18	0	1	0.0000000000000000D+00
powerf	0.2763966155009983D+00	0	1	0.0000000000000000D+00
denomf	0.3004462797974232D-01	0	1	0.0000000000000000D+00
tag1prefcf	-0.2203869703103454D-05	0	1	0.0000000000000000D+00
tag1 E0 f	0.2905286701571936D+00	0	1	0.0000000000000000D+00
tag1widthf	0.2264941897751681D+02	0	1	0.0000000000000000D+00
tag2prefcf	-0.4714532941632775D-05	0	1	0.0000000000000000D+00
tag2 E0 f	0.5148024308981736D+00	0	1	0.0000000000000000D+00
tag2widthf	0.2696316858620451D+02	0	1	0.0000000000000000D+00
interceptr	0.5128114882401200D-05	0	1	0.0000000000000000D+00
sloper	-0.2698631404472286D-06	0	1	0.0000000000000000D+00
prefacr	-0.1702483491473806D-18	0	1	0.1000000000000000D+01
powerr	0.2322032754702289D+00	0	1	0.1000000000000000D+01
denomr	0.3061830621889504D-01	0	1	0.1000000000000000D+01
tag1prefcr	0.2492001423663137D-05	0	1	0.0000000000000000D+00
tag1 E0 r	0.2772751906026441D+00	0	1	0.0000000000000000D+00
tag2prefcr	0.4604811466901315D-05	0	1	0.0000000000000000D+00
tag2 E0 r	0.4962647353455702D+00	0	1	0.0000000000000000D+00
nF/RT	0.3933730154289113D+02			
v start f	0.5000000000000000D-01			
v end f	0.6790000000000001D+00			
v start r	0.1000000000000000D-02			
v end r	0.6490000000000000D+00			
optfnc	0.1019655911099005D-05			
V shift	0.0000000000000000D+00			
tag1 area	0.973036E-07			
tag2 area	0.174851E-06			

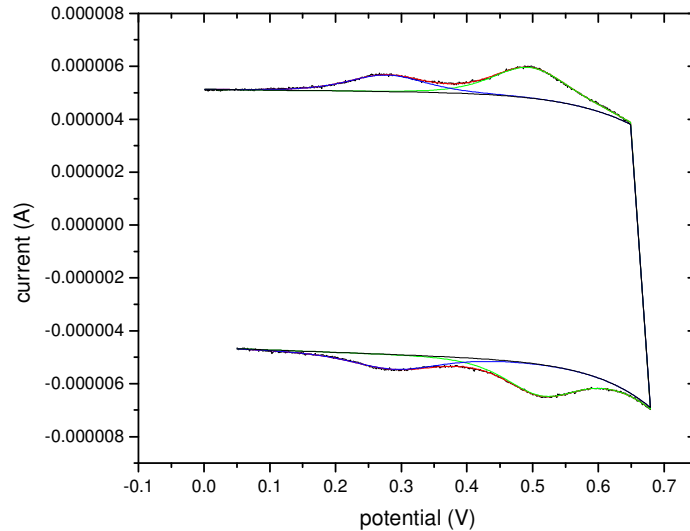


Figure 4.

The integrated tag areas are listed at the bottom of the fitdat file. These can also be calculated directly using equation 4. Note that it is not necessary for the entire peak to have been present in the experimental CV trace. This is because the program uses equation 4 rather than direct numerical integration to estimate the peak area; thus, as long as the prefc and width parameters of the peak can be estimated, the area can be calculated.

It is good practice to rerun the program once more with the fully optimized solution to double check that the best fit has indeed been found.