

Short Communication

Digital simulation of galvanostatic current–potential data for gas-diffusion electrodes and estimation of electrode-kinetic parameters

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(Received September 13, 1993; accepted January 13, 1994)

Abstract

A computerized non-linear-least-squares regression procedure to analyse the galvanostatic current–potential data for kinetically hindered reactions on porous gas-diffusion electrodes is reported. The simulated data fit well with the corresponding measured values. The analytical estimates of electrode-kinetic parameters and uncompensated resistance are found to be in good agreement with their respective values obtained from Tafel plots and the current-interrupter method. The procedure circumvents the need to collect the data in the limiting-current region where the polarization values are usually prone to errors. The polarization data for two typical cases, namely, methanol oxidation on a carbon-supported platinum–tin electrode and oxygen reduction on a Nafion-coated platinized carbon electrode, are successfully analysed.

Introduction

Porous electrodes that are commonly employed with fuel cells and batteries are routinely characterized by galvanostatic polarization studies. In an earlier publication [1], a method to estimate the electrode-kinetic parameters of gas-diffusion electrodes using the inflection point in the steady-state, current–potential curve was reported. Unlike the conventional procedure, this method does not require the steady-state, current–potential data close to the limiting-current values. This is important as such data are usually prone to experimental errors that arise from fluctuations in the steady-state values due to: (i) evolution of gases; (ii) shielding of the electrode surface by evolving gas bubbles to give an additional ohmic component, and (iii) interference from other reactions. Nevertheless, the graphical estimation of the electrode-kinetic parameters employed in this method is quite cumbersome, and could be erroneous if care is not taken to find slopes that represent changes in potential with current at various points of the current–potential curve. It was therefore considered worthwhile

to extract the electrode-kinetic parameters from the current-potential data by employing analytical mathematical packages that have become available with the advent of high-speed personal computers.

This communication describes a mathematical package that is used to derive the electrode-kinetic parameters from the galvanostatic steady-state current-potential data of certain gas-diffusion electrodes. This package makes the evaluation of electrode-kinetic parameters both simpler and faster than graphical methods.

Phenomenology and algorithm

A typical polarization curve for a gas-diffusion electrode is sigmoidal in shape and comprises three distinct regions. The first region belongs to the voltage drop at low currents and is due to the interface resistance. The second region is characterized by a linear drop with increasing current and is due to the intrinsic ohmic resistance of the electrolyte. The third region termed the 'diffusion-limited regime' and is represented by the final additional drop at high currents that arises from the depletion of acceptors at the interface for the transitory species. For such a situation, the current-potential behaviour under anodic Tafel conditions is given by [2, 3]:

$$\frac{i_a}{i_0} = \left(1 - \frac{i_a}{i_{1,a}}\right) \exp\left(\frac{n\alpha F}{RT} \eta\right) \quad (1)$$

where i_a is the measured current density, i_0 the exchange current density, $i_{1,a}$ the limiting current density, n the number of electrons involved in the rate-determining step (rds), α the anodic charge-transfer coefficient, $\eta = (E - E^0)$ the difference between the measured (E) and the reversible (E^0) values of the potential and F , R and T have their usual meaning.

Alternatively, eqn. (1) with the uncompensated ohmic component (R_u) is given by:

$$E = E^0 - \frac{RT}{n\alpha F} \ln \left[\frac{i_0(i_{1,a} - i_a)}{i_{1,a}i_a} \right] + i_a R_u \quad (2)$$

Equations (1) and (2) possess an inflection point at which the first derivative of potential with respect to the current (dE/di_a) is minimum for the anodic reactions. Consequently, the second derivative (d^2E/di_a^2) vanishes. Considering eqn. (2):

$$\frac{dE}{di_a} = \frac{RT}{n\alpha F} \frac{1}{i_a} + \frac{RT}{n\alpha F} \frac{1}{(i_{1,a} - i_a)} + R_u \quad (3)$$

and,

$$\frac{d^2E}{di_a^2} = \frac{RT}{n\alpha F} \left[\frac{1}{(i_{1,a} - i_a)^2} - \frac{1}{(i_a)^2} \right] \quad (4)$$

At the inflection point $i = i_{inf}$ and $d^2E/di_a^2 = 0$, consequently, $i_{1,a} = 2i_{inf}$. This relationship yields $i_{1,a}$ directly by determining the value of the current at the inflection point which corresponds to the minimum in the plot of dE/di_a versus $1/i_a$.

Subsequently, the kinetic parameters are obtained by recasting eqn. (3) in the following form:

$$\frac{dE}{di_a} = \frac{RT}{n\alpha F} \frac{1}{i_a} \frac{i_{1,a}}{(i_{1,a} - i_a)} + R_u \quad (5)$$

The plot of dE/di_a versus $i_{1,a}/(i_a(i_{1,a}-i_a))$ is a straight line with an intercept R_u and a slope $RT/n\alpha F$. The value of i_0 is obtained by substituting for R_u , $n\alpha$, $i_{1,a}$ in eqn. (2). Similar relationships could be written for an electrochemical process under cathodic Tafel conditions.

Alternatively, the electrode-kinetic parameters can be obtained analytically by a non-linear regression of the current-potential data using the algorithm described below. Generally, non-linear-least-squares regression uses a mathematical function of the form:

$$y=f(b_1, b_2, \dots, b_n, x) \quad (6)$$

where x is the independent variable, b_1, b_2, \dots, b_n are the parameters to be estimated, and y is the response value of the function, f . In the present case, y is taken as the electrode potential, E , at certain values x of the current, J . In a galvanostatic experiment, the electrode is loaded at various currents and the corresponding steady-state polarization potentials are recorded. In the algorithm, the current-potential input data is a $N \times 2$ matrix where N represents the total samples of J and E . The Tafel regime of the response polarization lies within the extremities where the current is represented by a Taylor series approximation of the polarization and the onset of mass polarization [2, 3]. Accordingly, the range of the data set for non-linear regression is fixed by:

$$i = 1, \dots, (N-k) \quad (7)$$

where k represents the total number of discarded J - E data.

The starting values of the independent variable, x , and the response function, y , are defined as $x=J_{i+l}$ and $y=E_{i+l}$ where l represents the discarded data points that pertain to the polarization region that is governed by a Taylor series approximation.

The algorithm for the non-linear regression of the current-potential data set comprises a matrix (M) with its columns equal to the number of unknown b parameters and an i number of rows. The columns in this matrix contain the array of data that correspond to the functional form chosen for the non-linear regression applied to the independent variable, x . The unknown b parameters are obtained from:

$$b = (M^T M)^{-1} (M^T y) \quad (8)$$

where M^T is the transpose of the matrix M . This facilitates evaluation of the function, f . The response function for an electrochemical reaction in the Tafel regime could be taken as: $f(x) = b_1 + b_2 x + b_3 \frac{\ln(x)}{\sqrt{y_i - f(x_i)}}$. The best fit of the regression is determined by least-squares deviation: $\delta = \sum_i \sqrt{(y_i - f(x_i))^2}$, or the mean-squared error is given by:

$$\delta / (\text{length}(y) - \text{length}(b)).$$

Case studies

In order to examine the feasibility of the model and the adaptability of the non-linear regression for the estimation of electrode-kinetic parameters, two typical case studies of kinetically hindered reactions occurring on porous gas-diffusion electrodes have been undertaken. The first case study involves methanol oxidation on a carbon-supported platinum-tin catalyzed electrode in sulfuric acid electrolyte [4], while the other is concerned with the oxygen-reduction reaction at a Nafion-coated gas-diffusion electrode that is composed of a carbon-supported platinum catalyst [5].

The mathematical package for methanol oxidation on a carbon-supported platinum-tin catalyzed electrode is presented in the Appendix. Computation was carried

out by using the Mathematica™ software package [6,7] in an interactive mode. According to the method described above, a non-linear-least-squares regression was used to fit the measured data (Figs. 1 and 2). The base function employed for the analysis is obtained by combining the Volmer–Butler equation (corrected for both the mass transport and the ohmic components of polarization [2, 3]) with a polynomial function. The latter takes into account deviations from the theoretical behaviour that arise from the presence of secondary reactions at high overpotentials and also from fluctuations in the experimental data (Fig. 2). The regression ranges and plot limits are at the option of the user as these change from situation to situation. The method provides satisfactory fitting to the input data. The precision of the data fitting is estimated from the mean-squared error. Derivative functions of the simulated curve are then obtained analytically (Figs. 3 to 5). The intersection on the abscissa of the second

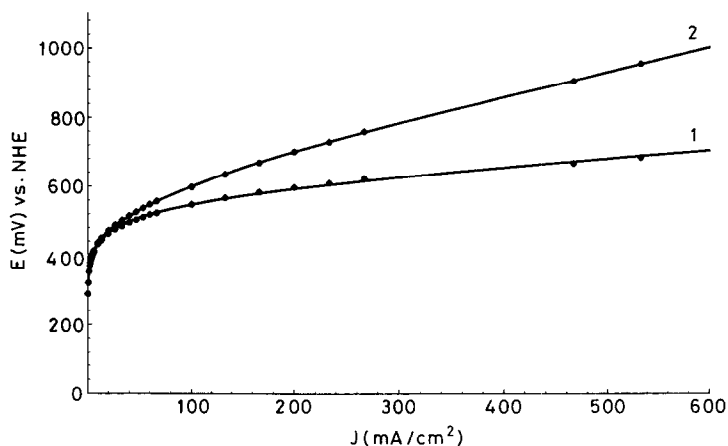


Fig. 1. Experimental current–potential data for methanol oxidation on a carbon-supported platinum–tin electrode in sulfuric acid electrolyte at 60 °C: curve 1 with, and curve 2 without ohmic correction.

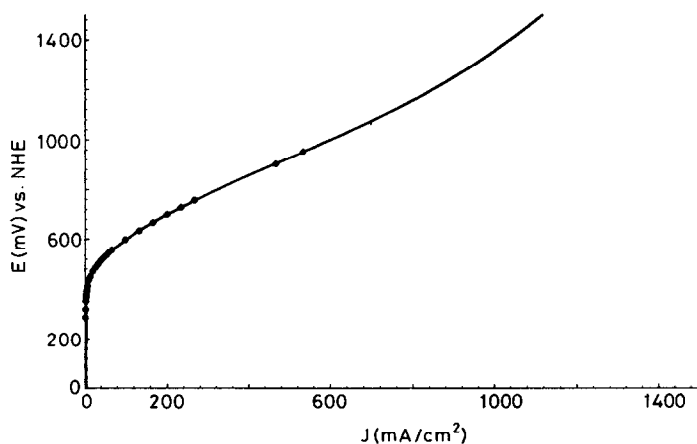


Fig. 2. Comparison of (full line) simulated current–potential data with (filled squares) experimentally obtained values for methanol oxidation.

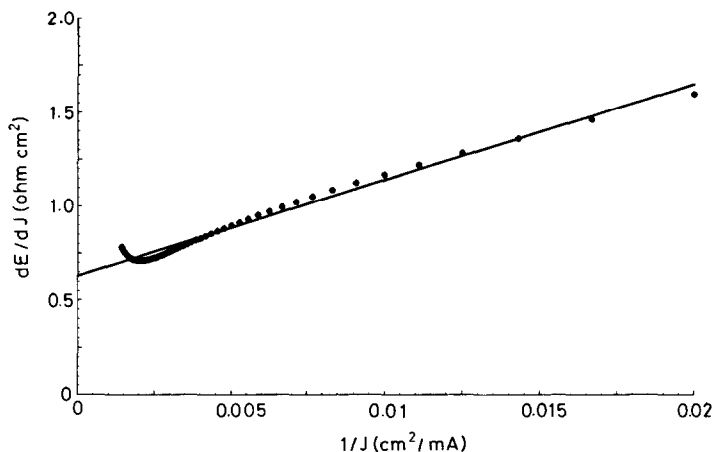


Fig. 3. Simulated first derivative (dE/dJ) of potential (E) with respect to current, J , vs. $1/J$ for methanol oxidation.

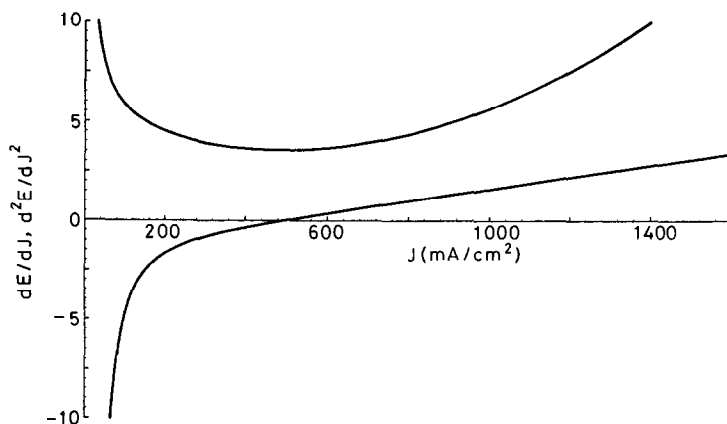


Fig. 4. Simulated dE/dJ and d^2E/dJ^2 vs. current, J , for methanol oxidation.

derivative function (Fig. 4) gives the inflection point which yields the value of the limiting current. Linear regression of the derivative of simulated curve versus the inverse of current gives the electrode-kinetic parameters ($n\alpha$) and the uncompensated resistance (R_u). The estimated R_u values are found to be in close agreement with those obtained experimentally by the current-interrupter method. Furthermore, the electrode-kinetic parameter ($n\alpha$) is close to its value obtained from the Tafel plot subsequent to the correction for mass transfer of the data (Fig. 6). This confirms the feasibility of the present regression procedure. The overall process of calculation and rendering in post-script of the plots takes about 30 s on a PC 80486 IntelTM microprocessor equipped with 16 Mbyte RAM memory.

The representative data for oxygen reduction on a Nafion-coated platinized carbon electrode corresponding to Figs. 2, 5 and 6 for methanol oxidation are shown in Figs. 7 to 9, respectively. In this case study, there are two distinct Tafel regimes. Accordingly, the regression had to be carried out in two current-potential regions of

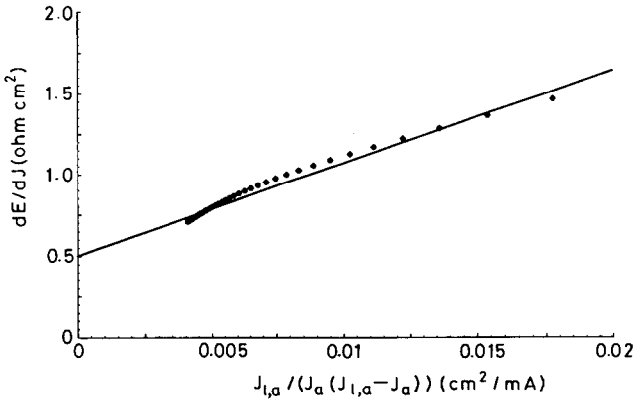


Fig. 5. Simulated dE/dJ vs. $J_{i,a}/(J_a(J_{i,a}-J_a))$ for methanol oxidation.

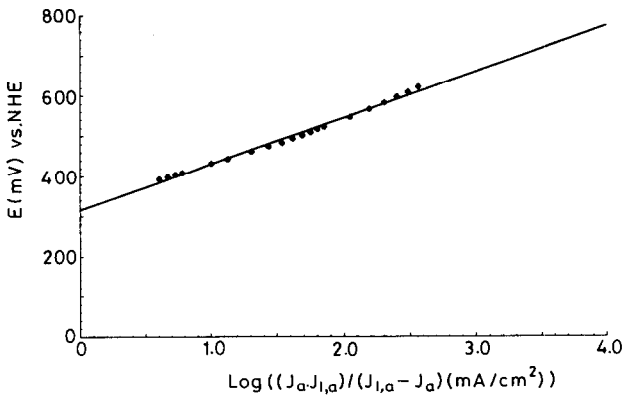


Fig. 6. Tafel plots for methanol oxidation.

the polarization data. The estimated values of electrode-kinetic parameters are found to be in good agreement with those reported in a study employing microelectrodes [8]. The estimated values of uncompensated resistance are also close to those obtained experimentally.

A comparison between the values of electrode-kinetic parameters obtained from the Tafel plot and those derived from the simulated data for both the case studies are presented in Table 1.

Conclusions

An advantage of the present digital simulation of steady-state galvanostatic data for gas-diffusion electrodes is the analytical evaluation of the limiting current that circumvents the need to reach the current-potential region where secondary reactions can vitiate the data. The analysis is also useful for situations where large ohmic drops occur at the electrode/electrolyte interface since the uncompensated resistance is directly obtained from the simulated data by using the linear regression procedure. It is noteworthy that the correction of current-potential data both for mass transfer and

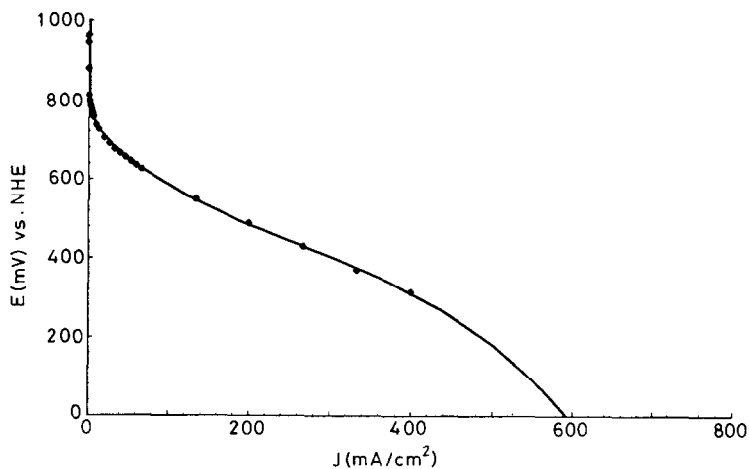


Fig. 7. Comparison of simulated current-potential data for oxygen reduction on a Nafion-coated platinumized-carbon electrode at 60 °C with experimentally observed data.

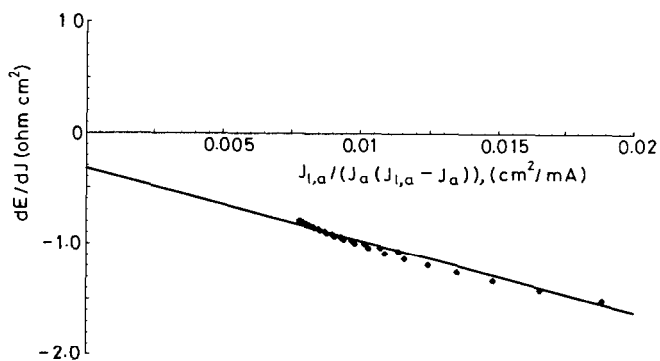


Fig. 8. Simulated dE/dJ vs. $J_{l,c}/(J_{l,c} - J_c)$ for oxygen reduction.

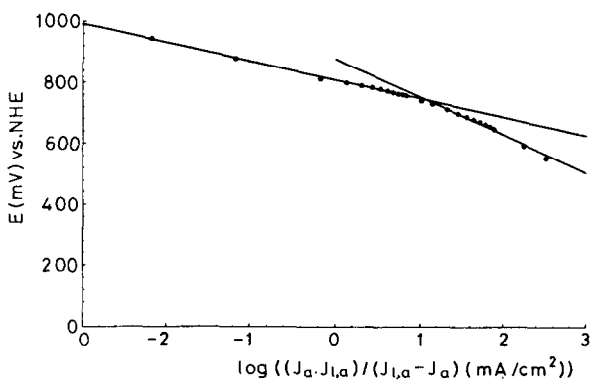


Fig. 9. Tafel plots for oxygen reduction.

TABLE 1. Electrode-kinetic parameters and R_u values

Case study	Simulated curve		Tafel plot		Simulated R_u ($\Omega \text{ cm}^2$)	Measured R_u ($\Omega \text{ cm}^2$)	i_{inf} (mA cm^{-2})
	$n\alpha_1$	$n\alpha_2$	$n\alpha_1$	$n\alpha_2$			
Methanol oxidation	0.49		0.57		0.50	0.51	490.85
Oxygen reduction reaction	1.00	0.43	1.08	0.53	0.33	0.32	256.32

ohmic components of polarization is important in deriving the electrode-kinetic parameters for reactions on gas-diffusion electrodes. The present non-linear regression analysis provides more accurate and stable results in relation to the graphical approach. It is fast and can be easily performed using readily available mathematical packages on microcomputers.

Acknowledgement

Our thanks are due to G. Candiano for his assistance.

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Appendix

Input datafile (V is equivalent to E), corrections for electrode geometric area (1.5 cm²), SCE (242 mV vs. NHE) and experimentally measured R_u (0.51 $\Omega \text{ cm}^2$); interpolation of the data

```

datainput = ReadList ["PtSnfile. txt", {Number, Number}];
Jin = Transpose[datainput] [[1]]; J = Jin/1.5;
Vin = Transpose[datainput] [[2]]; V = Vin + 242;
datamod = {J,V}; data = Transpose[datamod];
Ru = 0.51; Vr = V - J Ru; N1 = Length [J];

```



```

data1 = Take[data, {5, N1}];
mmod = {J, Vr}; m = Transpose[mmod]; m1 = Take[m, {5, N1}];
hy = Append[Table[x^i, {i, 0, 1}], Log[x]];
f1 = Fit [data1, hy, x];
f2 = Fit [m1, hy, x];

```

Plot of experimental and ohmic corrected data

```

Show [Plot [f1, {x, 1, 600}, DisplayFunction -> Identity],
Plot[f2, {x, 1, 600}, DisplayFunction -> Identity],
ListPlot[data, DisplayFunction -> Identity],
ListPlot[m1, DisplayFunction -> Identity],
PlotRange -> {{0, 600}, {0, 1100}},
AxesLabel -> {"J (mA/cm2)", "E(mV)vs.NHE"},
DisplayFunction -> $DisplayFunction];
See Fig. 1 for plot.

```

Non-linear-least-squares fitting of data

```

N1 = Length[data];
data1 = Take[data, {10, N1}];
hy2 = Append[Table [x^i, {i, 0, 3}], Log[x + (10^i - 13)]];
f1 = Fit[data1, hy2, x];

```

Plot of simulated data

```

p3 = Plot[f1, {x, 0, 1500}, DisplayFunction -> Identity];
p4 = ListPlot [data, DisplayFunction -> Identity];
Show[p3, p4, PlotRange -> {{0, 1500}, {0, 1500}},
AxesLabel -> {"J (mA/cm2)", "E(mV)vs.NHE"},
DisplayFunction -> $DisplayFunction]
See Fig. 2. for plot.

```

Derivatives of simulated curve

```

t = D[f1, x];
m = Table[t, {x, 50, 700, 10}]; xx = Table[1/x, {x, 50, 700, 10}]/N;
g = {xx, m}; gg = Transpose[g]; ggg = Reverse[gg];
l = Fit[ggg, {1, xxx}, xxx];

```

Plot of derivative function of simulated curve versus inverse of current

```

p6 = Plot[l, {xxx, 0, 0.02}, DisplayFunction -> Identity];
p5 = ListPlot[ggg, DisplayFunction -> Identity];
Show[p5, p6, PlotRange -> {{0, 0.02}, {0, 2}},
AxesLabel -> {"1/J (cm2/mA)", "dE/dJ (ohm cm2)"},
DisplayFunction -> $DisplayFunction]
See Fig. 3 for plot.

```

Electrode-kinetic parameters (n) and R_u as obtained from simulated data

```

n1 = 28/(D[1, xxx]0.5)
1.09204161409148 (represents the number of electrons involved in the rds)
1
0.6297314787758037 + 51.28009709280995*xxx
(represents Ru and slope, respectively)

```

Limiting current (Jl) as obtained from simulated data

```

t2 = D[f1, {x, 2}];
Solve[t2 = 0, x];

```

```
b = Last[%];
infl = x/.%
490.8535467839074 (represents current at the inflection point)
```

Derivatives of simulated curves

```
p11 = Plot[t2*1000, {x, 0, 1600}, DisplayFunction → Identity];
p12 = Plot[t*5, {x, 0, 1600}, DisplayFunction → Identity];
Show[p11, p12, PlotRange → {{0, 1600}, {-10, 10}},
AxesLabel → {"J", "dE/dJ, d2E/dJ2"},
DisplayFunction → $DisplayFunction]
See Fig. 4 for plot.
```

Electrode parameter (n) subsequent to mass-transport correction and estimation of R_u

```
ilim = 2*infl; mm = Table[t, {x, 50, 600, 10}];
xa = Table[(ilim/(x*(ilim-x))), {x, 50, 600, 10}]/N;
ga = {xa, mm}; gga = Transpose[ga];
gga2 = Reverse[gga];
l2 = Fit[gga2, {1, x^4}, x^4]
0.50242458017527 + 56.93703475715085*x^4
(represents  $R_u$  and slope, respectively, subsequent to mass-transport correction)
n2 = 28/(D[l2, x^4] 0.5)
0.9835426140271 (represents the number of electrons
involved in the rds, subsequent to mass-transport correction)
```

Mass-transport corrected derivative function of simulated curve

```
p18 = Plot[l2, {x^4, 0, 0.02}, DisplayFunction → Identity];
p19 = ListPlot[gga2, DisplayFunction → Identity];
Show[p18, p19, PlotRange → {{0,0.02}, {0,2}},
AxesLabel → {"J1/(J(J1 - J)) (cm2/mA)",
{"dE/dJ (ohm cm2)"},
DisplayFunction → $DisplayFunction]
See Fig. 5 for plot.
```

Tafel analysis of data subsequent to mass transport and ohmic correction

```
Jl = ilim; J1 = Take[J, {7, 26}]; Jm = ((J1*J1)/(J1-J1));
JJm = Log[10, Jm]; VVr = Take[Vr, {7, 26}];
lim = {JJm, VVr}; lim1 = Transpose[lim];
ll1 = Fit[lim1, {1, x}, x];
n3 = 66/(D[ll1, x] 0.5)
1.147399724752915 (represents the number of electrons involved in the rds)
ppp1 = ListPlot[lim1, DisplayFunction → Identity];
pp2 = Plot[ll1, {x, 0, 4}, DisplayFunction → Identity];
Show [pp1, pp2, PlotRange → {{0, 4}, {0, 800}},
AxesLabel → {"Log((J-J1)/(J1-J) (mA/cm2)",
{"E (mV) vs. NHE"}},
DisplayFunction → $DisplayFunction];
See Fig. 6 for plot.
```