

## INFLUENCE OF ELECTRODE GEOMETRY AND NLLS FIT ANALYSIS OF $I$ - $V$ MEASUREMENTS IN A THREE-ELECTRODE CELL

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The analysis of electrode polarisation ( $I$ - $V$ ) measurements of oxygen electrodes on  $\delta$ - $\text{Bi}_2\text{O}_3$ -based solid electrolytes is complicated by an ohmic polarisation correction which is of the order of the electrode resistance. The analysis can be performed with a NLLS fit technique, which includes this correction resistance,  $R_u$ , as adjustable parameter. By an appropriate choice of the electrode geometry the factor  $R_u$  can be minimized.

### 1. Introduction

The application of oxygen ion conducting solid electrolytes in electrochemical devices, such as fuel cells, oxygen pumps and electro-catalytic reactors, depends on the availability of good, stable oxygen electrodes that exhibit high exchange currents. Recent results on  $\delta$ - $\text{Bi}_2\text{O}_3$ -based solid electrolytes have shown that these materials have a high surface oxygen exchange current, independent of the type of (noble) metal electrode applied [1].

The properties of these porous gold and platinum electrodes and of thin mixed conducting oxide electrodes on such electrolytes are measured in a three-electrode cell [2-5] allowing the anodic and cathodic polarisation to be measured separately. In most cases the current-overvoltage relation can be expressed in terms of the Butler-Volmer equation (BV),

$$I = I_0 [\exp(\alpha_a n F \eta / RT) - \exp(-\alpha_c n F \eta / RT)], \quad (1)$$

where  $n$  is the number of times the rate determining step has to occur for the complete reaction to take place,  $\alpha_a$  and  $\alpha_c$  are the exchange coefficients, with  $\alpha_a + \alpha_c = 1$ , and  $\eta$  is the actual overpotential of the electrode, which is measured with respect to a (currentless) reference electrode. Because of the current flux lines between the work and counter electrode and the position of the reference electrode an ohmic

potential drop exists between the reference and work electrode for which  $\eta$  must be corrected.

$$\eta = V - IR_u. \quad (2)$$

$V$  is the actual voltage measured between work and reference electrodes.  $R_u$  depends in principle on the bulk resistivity of the electrolyte and the geometric arrangement of the electrodes. In many cases  $R_u$  can be neglected with little error as it is small compared to the electrode resistance,  $R_c$ ,

$$R_c = dV/dI|_{V=0} = RT/nFI_0. \quad (3)$$

For the currently investigated Bi-containing electrolytes [1,6] the exchange currents are so high that  $R_c$  becomes of the same order of  $R_u$  in magnitude and thus the correction critically influences the calculated parameters for the BV equation. To improve this situation one can optimise the electrode geometry and obtain the  $R_u$  from ac impedance measurements in the three-electrode cell.

Due to the limited voltage range that can be applied to these materials, the anodic branch of the polarisation often does not reach, after correction for  $R_u$ , into the linear region in the Tafel plot ( $\ln|I|$  versus  $\eta$ ). This can be overcome by analysing the  $I$ - $V$  data with a NLLS fit procedure which includes  $R_u$  as adjustable parameter. The potential of the NLLS fitting techniques has recently been demonstrated in

impedance spectroscopy and is recognised as a powerful tool in data analysis [7,8].

## 2. Optimizing the electrode geometry

On thin, disc-shaped samples the work electrode and the (noble metal) reference electrode are situated on one side of the sample. For practical reasons a well-defined, annular-shaped work electrode is used with the reference point electrode in its center, while the opposite face of the solid electrolyte disc is almost covered with a full circular counter electrode. A two-dimensional simulation for this arrangement, using conductive paper, shows that the potential of the reference electrode approaches the counter electrode potential (fig. 1A). Using also an annular-shaped counter electrode increases the reference electrode potential above half the difference between the counter and work electrode (fig. 1B), and consequently decreases  $R_u$ . The value of  $R_u$  depends strongly on the ratio of the inner radius,  $r_a$  of the annular electrode and the thickness of the sample. Therefore it is advisable to decrease  $r_a$  as much as is practically feasible.

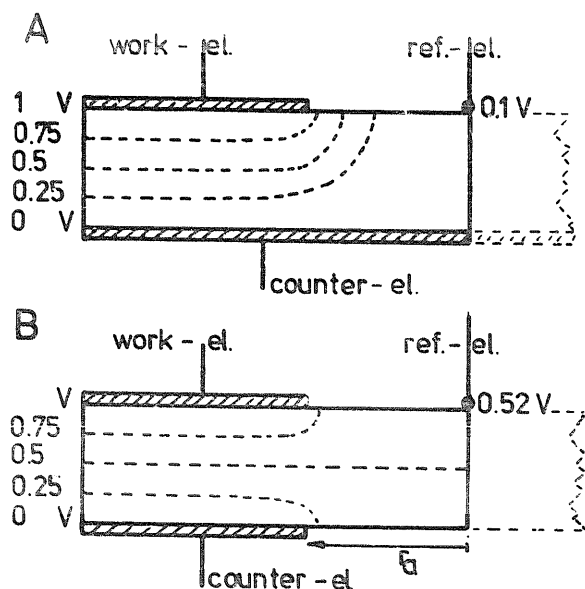


Fig. 1. Schematic two-dimensional model for the equipotential lines for (A) a full counter electrode, and (B) an annular counter electrode. Results are obtained with conductive paper.

## 3. NLLS fit procedure

Fitting a model function  $F(x, a_j)$ ,  $j=1, \dots, m$ , to a set of measured data,  $x_i, y_i, i=1, \dots, N$ , is a well-known procedure. A large variety of NLLS fitting routines are available in program libraries, both for main frame and personal computers. In such a procedure, the weighted error sum

$$S = \sum_{i=1}^N w_i [y_i - F(x_i, a_j)]^2 \quad (4)$$

is minimised by simultaneously adjusting the parameters  $a_j$  of the fitting function. As  $F(x, a_j)$  is generally not linear in its parameters, it is linearised through a Taylor series development around a set of starting values,  $a_j^0$ , ignoring higher-order terms. By setting the partial derivatives of the error sum with respect to the parameters,  $\partial S / \partial a_j$ , to zero, a set of  $m$  linear equations is obtained. In matrix form:

$$\alpha \cdot \hat{a} = \beta \quad (5)$$

with

$$\alpha_{m,k} = \sum_{i=1}^N w_i \frac{\partial F(x_i, a_j)}{\partial a_m} \frac{\partial F(x_i, a_j)}{\partial a_k} \quad (6)$$

and

$$\beta_k = \sum_{i=1}^N w_i [y_i - F(x_i, a_j)] \frac{\partial F(x_i, a_j)}{\partial a_k}. \quad (7)$$

By multiplying both sides with the inverse of matrix  $\alpha$ ,  $\epsilon = \alpha^{-1}$ , the solution is found. This results in a new, improved set of (starting) parameters. This iterative procedure is continued until the change in the parameters becomes insignificant [7,9].

For the  $I-V$  measurements the fit function becomes the modified Butler-Volmer equation, with  $A = nF/RT$ ,

$$I = I_0 \{ \exp[\alpha_a A (V - IR_u)] - \exp[-(1 - \alpha_a) A (V - IR_u)] \}, \quad (8)$$

which imposes a problem as it cannot be expressed simply in terms of a fit function,  $F(V, \alpha_a, I_0, R_u)$ , because  $I$  appears in both exponents on the right-hand side of eq. (8). The evaluation of  $I$  for a set of  $\alpha_a, I_0, R_u$  at a specified voltage,  $V$ , can be obtained, however, through an iterative procedure. For this a new function,  $f(I)$ , is defined:

$$f(I) = I - I_0 \{ \exp[\alpha_a A(V - IR_u)] - \exp[-(1 - \alpha_a)A(V - IR_u)] \}. \quad (9)$$

For  $f(I) = 0$  the correct value for  $I$  is found. The root of  $f(I)$  can be obtained using a Newton-Raphson iteration. For a starting point,  $I'$  on  $f(I)$  the tangential line is drawn. The intersection of this line with the  $I$ -axis gives a new improved value,  $I''$ ,

$$I'' = I' - f(I') [df(I)/dI|_{I=I'}]. \quad (10)$$

This iteration is carried out until the change in  $I$  becomes insignificant.

The NLLS fit procedure also requires the partial derivatives with respect to the parameters  $\alpha_a$ ,  $I_0$ ,  $R_u$  of  $I(V)$ , (eqs. (6,7)). These can be obtained directly from the modified BV, eq. (8). E.g. for  $\partial I/\partial I_0$ ,

$$\partial I/\partial I_0 = (e^+ - e^-) - I_0 [\alpha_a AR_u \partial I/\partial I_0 + e^-(1 - \alpha_a)AR_u \partial I/\partial I_0] \quad (11)$$

with

$$e^+ = \exp[\alpha_a A(V - IR_u)], \quad e^- = \exp[-(1 - \alpha_a)A(V - IR_u)]. \quad (12)$$

Bringing  $\partial I/\partial I_0$  to the left-hand side results in

$$\partial I/\partial I_0 = (e^+ - e^-)/Q, \quad (13)$$

with

$$Q = 1 + I_0 AR_u [\alpha_a e^+ + (1 - \alpha_a) e^-]. \quad (14)$$

In the same way the other two partial derivatives are found:

$$\partial I/\partial \alpha_a = I_0 A(V - IR_u) (e^+ - e^-)/Q \quad (15)$$

and

$$\partial I/\partial R_u = -I_0 IA [\alpha_a e^+ + (1 - \alpha_a) e^-]/Q. \quad (16)$$

With this set of formulas the NLLS fit can easily be programmed on a personal computer.

The fit procedure requires a set of starting values for the adjustable parameters. This can readily be automated as only one function is used in the analysis. For most of the oxygen electrodes on solid electrolytes the anodic polarisation is much less than the cathodic one. As a consequence, the influence of  $R_u$  is noticed mostly in the anodic branch. Hence the slope at the high voltage limit of the anodic branch

of the  $I-V$  curve gives an estimate for  $R_u$ , while the slope of the curve at  $V=0$  gives the sum of  $R_c$  and  $R_u$ :

$$dI/dV|_{V \rightarrow \infty} = 1/R_u, \quad dI/dV|_{V=0} = 1/(R_u + R_c). \quad (17)$$

Using eq. (3) an estimate for  $I_0$  is obtained from  $R_c$ , while the temperature and  $n$  are specified by the user. The estimate for  $\alpha_a$  is obtained from the Tafel slope of the cathodic branch, after correction for  $R_u$ . The quality of the starting values obtained thus generally allows a simple analytical NLLS fit, which converges faster than the Marquardt NLLS fit procedure [8,10]. An added advantage of this fit procedure is that under certain assumptions error estimates may be obtained for the parameters from the error matrix,  $e$  [7].

#### 4. Four-parameter fit procedure

In quite a number of  $I-V$  measurements, performed with porous gold electrodes on  $(\text{Bi}_{0.75}, \text{Er}_{0.25})_2\text{O}_3$  electrolyte (BE25), it was obvious that integer values for  $n$  did not result in adequate fits [6]. Because of this the fit procedure was augmented to include also the parameter  $n$ . For practical reasons the anodic and cathodic exchange coefficients were then defined as

$$\alpha'_a = \alpha_a n \quad \text{and} \quad \alpha'_c = \alpha_c n = (1 - \alpha_a) n. \quad (18)$$

Also the derivatives must be modified and extended:

$$\partial I/\partial \alpha_a = I_0 A(V - IR_u) e^+/Q, \quad (19)$$

$$\partial I/\partial \alpha_c = I_0 A(V - IR_u) e^-/Q, \quad (20)$$

$$\partial I/\partial I_0 = (e^+ - e^-)/Q \quad (21)$$

and

$$\partial I/\partial R_u = -I_0 IA (\alpha_a e^+ + \alpha_c e^-)/Q, \quad (22)$$

with

$$Q = 1 + I_0 AR_u (\alpha_a e^+ + \alpha_c e^-). \quad (23)$$

The results of the three-parameter fit present excellent starting values for a subsequent four-parameter fit procedure, which then only requires an analytical fit procedure.

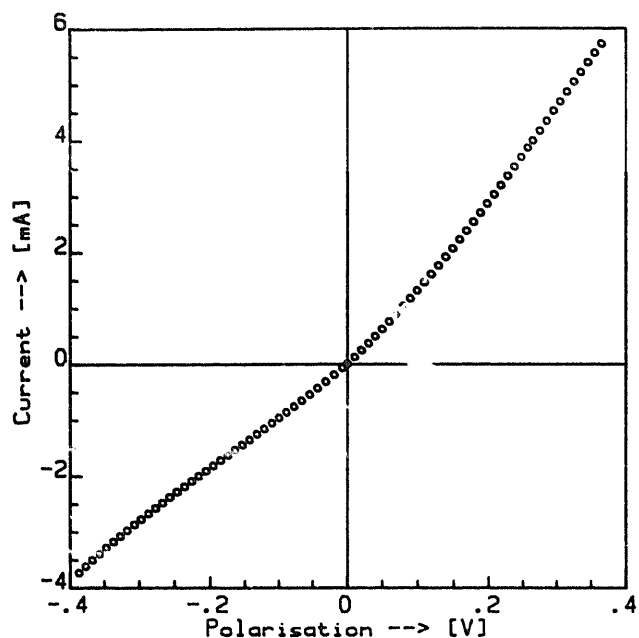


Fig. 2.  $i$ - $V$  curve for a porous gold electrode on  $(\text{Bi}_{0.75}, \text{Er}_{0.25})_2\text{O}_3$  in oxygen at 917 K. This curve presents a "worst case curve" where  $R_c \approx R_u$ .

## 5. Results and discussion

Fig. 2 shows a good example of  $i$ - $V$  data where  $R_c$  is of the same magnitude as  $R_u$ . The data are taken from a  $(\text{Bi}_{0.75}, \text{Er}_{0.25})_2\text{O}_3$  sample with porous gold electrodes in oxygen at 917 K [6]. The results of a three parameter fit for  $n=2$  and  $n=3$ , and for a four-parameter fit with error estimates are given in table 1. The value,  $n=2.6$ , obtained from the four-parameter fit is tentatively interpreted as a competition between a charge-transfer-limited process ( $n=2$ ) and

Table 1

Results for a three- and four-parameter NLLS fit procedure for the data of fig. 2. For the three-parameter fit the value of  $n$  was specified. Unity weight factors were used in all fit procedures.

Parameter	Three-parameter NLLS fit		Four-parameter NLLS fit with estimated error
	$n=2$	$n=3$	
$\alpha_a$	0.75	0.79	$0.77 \pm 0.03$
$\alpha_c$	0.25	0.21	$0.23 \pm 0.01$
$n$	(2)	(3)	$2.57 \pm 0.08$
$I_0$ (A)	9.7	7.9	$(8.5 \pm 0.2) \times 10^{-4}$
$R_u$ (ohm)	46.4	51.9	$50.0 \pm 0.5$
$R_c$ (ohm)	40.7	33.4	$36.2 \pm 1.4$

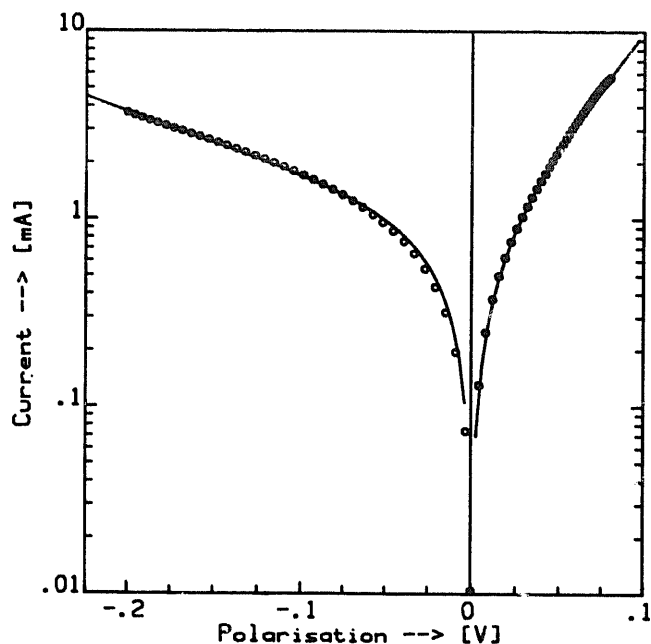


Fig. 3. Tafel plot, corrected for  $IR_u$ , of the  $i$ - $V$  data of fig. 2. The solid line represents the result of the four-parameter NLLS fit.

a diffusion-limited process [6]. Apparent non-integer values for  $n$  have also been found for Pt electrodes on  $\text{Y}_2\text{O}_3$  stabilised  $\text{ZrO}_2$  [11].

The correctness of the fit is best observed in the (for  $IR_u$  corrected) Tafel plot of fig. 3. It is obvious that the choice of  $R_u$  will strongly influence the observed value for  $n$ , obtained from a simple graphical analysis in a corrected Tafel plot. The weight factors were set to 1, assuming that the statistical errors in the measured data are independent of the current or voltage. The reproducibility of the fit results for identical measurements was found to be excellent. The spread in the calculated parameters was close to the calculated error estimates from the NLLS fits.

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