Evaluation of the BEASY program using linear and piecewise linear approaches for the boundary conditions

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The boundary element method (BEM) was used to study galvanic corrosion using linear and logarithmic boundary conditions. The linear boundary condition was implemented by using the linear approach and the piecewise linear approach. The logarithmic boundary condition was implemented by the piecewise linear approach. The calculated potential and current density distribution were compared with the prior analytical results. For the linear boundary condition, the BEASY program using the linear approach and the piecewise linear approach gave accurate predictions of the potential and the galvanic current density distributions for varied electrolyte conditions, various film thicknesses, various electrolyte conductivities and various area ratio of anode/cathode. The 50-point piecewise linear method could be used with both linear and logarithmic polarization curves.

1 Introduction

The study of the galvanic corrosion of magnesium is becoming increasingly important as the use of magnesium rapidly increases. Magnesium alloys are the lightest structural metals and are considered to be promising alternatives to aluminium alloys for automotive components due to their low density and high strength/weight ratio. The corrosion of magnesium alloys, however is one of the main concerns that limits the application of magnesium in industry [1]. Corrosive attack may occur via a number of different mechanisms. Of these, galvanic corrosion is probably the most important for magnesium because magnesium is the most anodic engineering metal and consequently corrodes at an accelerated rate when joined to the other common metals of construction, such as aluminium or steel. In order to reduce galvanic corrosion, it is useful to conduct a detailed analysis of galvanic corrosion occurring on the surface of a magnesium component coupled with a component made from a dissimilar metal.

Numerical methods have been demonstrated to be powerful tools in the analysis of corrosion problems in the last two decades. Numerical methods applied to galvanic corrosion studies have included the finite difference method (FDM), the finite element method (FEM) and the boundary element method (BEM). The BEM has the distinct advantage over the other two methods in that only the domain boundary of interest is required to be discrete. BEM needs fewer equations and a smaller matrix size than FEM and can solve both finite and infinite domain problems. The BEM is the most flexible and was the focus of this study.

Application of numerical methods to model galvanic corrosion requires use of the proper expression for the relationship between the potential and current density. Linear expressions and non-linear expressions have been used in the prior studies [2–8]. Typical polarization curves for magnesium indicated that the current and potential obey a non-linear relationship. This non-linear relationship must be used if the BEM is to be applied to the galvanic corrosion problem. Various curve fitting approaches have been reviewed by *Munn* [5]. The curve fitting approach required a complicated procedure to reduce the convergence problem and required additional parameters to allow equations to be inverted. Particularly for the more complicated 3-D geometry, no relevant commercial program has been reported. Therefore, a piecewise linear approach to the non-linear polarization curve was used in this study. It was assumed that any curve could be approximated as a combination of a series of small linear segments. This piecewise linear method was implemented using the commercial program BEASY. Furthermore, BEASY provides the facility to develop a user-programmable interface to implement various boundary conditions and BEASY has the ability to handle large, geometrically complex problems.

The purpose of this paper was to evaluate the accuracy of BEASY calculations using linear and piecewise linear boundary conditions. The approach taken was to compare the BEASY calculations against prior modelling results. This paper also investigated the ability of the BEASY program to conduct galvanic corrosion modelling by investigating the influence of the change in electrolyte properties, galvanic cell dimensions and the polarization behaviour.

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2 Theory

2.1 Galvanic current density distribution in electrolyte

The initial steady state current density distribution is produced as a result of the solution resistance and the potential difference between the anode and the cathode metal surfaces. The corrosion potentials of magnesium and steel in the same electrolyte are different, which causes a current to flow through the electrolyte when the metals are brought into contact.

The equation governing the current flow and the potential distribution in the electrolyte can be derived from first principles. The continuity equation (charge conservation) requires that the current per unit volume I relates to the charge q by [9]:

$$-\nabla I = \frac{\partial q}{\partial t} \tag{1}$$

For a system in steady state, $\partial q/\partial t = 0$. Taking into account the relationship of electric field intensity, E,

$$E = -\nabla \phi, \tag{2}$$

and Ohms law

$$I = KE, \tag{3}$$

where K is the conductivity of the electrolyte. The continuity equation transforms to

$$\nabla K \nabla \phi = 0. \tag{4}$$

For an electrolyte with uniform, isotropic conductivity, K is a constant, so that,

$$\nabla^2 \phi = 0, \tag{5}$$

Therefore, for a uniform, isotropic electrolyte, the potential obeys the equation (5) which is the Laplace equation. The current density, at any point inside the electrolyte can be evaluated by:

$$I_{xi} = -K \frac{\partial \phi}{\partial x_i} \tag{6}$$

where I_{xi} is the current density in the x_i direction, ϕ is the potential.

2.2 Boundary element method

The mathematical formulation has been described by *Adey* [10] for a uniform, isotropic electrolyte domain Ω as illustrated in Fig. 1. The Laplace equation (equation (5)) is solved using the following boundary conditions:

$$\phi = \phi_0, \quad \text{on } \Gamma_1, \tag{7}$$

$$I = I_0, \quad \text{on } \Gamma_2, \tag{8}$$

$$I_a = f_a(\phi), \quad \text{on } \Gamma_{3a}, \tag{9}$$

$$I_c = f_c(\phi), \quad \text{on } \Gamma_{3c}, \tag{10}$$

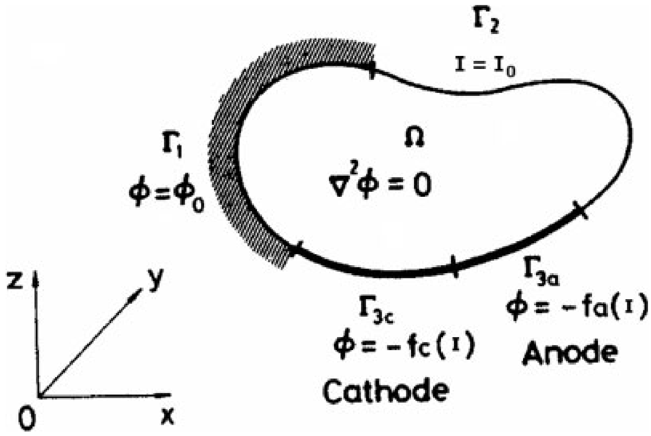

Fig. 1. Basic equations and boundary conditions for the application of BEM to galvanic corrosion

where Γ ($\equiv \Gamma_1 + \Gamma_2 + \Gamma_{3a} + \Gamma_{3c}$) is the entire surface of the electrolyte domain Ω, I is the current density across the boundary, and ϕ is the potential. ϕ_0 and I_0 are given constant values of potential and current density respectively. $f_a(\phi)$ and $f_c(\phi)$ are linear or non-linear functions that describe the anode and cathode electrode kinetics respectively.

When using the boundary method to solve the Laplace equation, the residual weighting function is chosen to minimize the error. The boundary integral expression was derived as equation (11) by reducing the integral equation [10].

$$c(y)\phi(y) + \int_\Gamma \phi(x) I^* (y,x) d\Gamma(x) = \int_\Gamma I(x)\phi^* (y,x) d\Gamma(x) \tag{11}$$

where ϕ^* and I^* are the fundamental solutions. The boundary of the electrolyte is divided into fine boundary elements that are non-overlaping and cover the whole of the boundary. Equation (11) can be rewritten as

$$c_i\varphi_i + \int_\Gamma \phi I^* \, d\Gamma = \int_\Gamma I\phi^* \, d\Gamma \tag{12}$$

Since Γ has been approximated by N elements, equation (12) becomes

$$c_i\phi_i + \sum_{j=1}^{N} \int_{\Gamma j} \phi I^* \, d\Gamma = \sum_{j=1}^{N} \int_{\Gamma j} I\phi^* \, d\Gamma \tag{13}$$

where $\int_{\Gamma j}$ denotes integration over element j. The equations for all elements can be assembled into a system of linear simultaneous equations, which is expressed in a matrix form as follows:

$$H\,\phi = G\,I \tag{14}$$

where H and G are problem influence matrices, and ϕ and I represent potential and current density vectors respectively. The size of the system of equations is defined by the number of nodes. Partitioning the ϕ and I into those nodes which form the anode and the cathode regions and applying the boundary condition of equation (9) and equation (10), gives

$$\begin{bmatrix} h_{aa} & h_{ac} \\ h_{ca} & h_{cc} \end{bmatrix} \begin{bmatrix} \phi_a \\ \phi_c \end{bmatrix} = \begin{bmatrix} g_{aa} & g_{ac} \\ g_{ca} & g_{cc} \end{bmatrix} \begin{bmatrix} f_a(\phi_a) \\ f_c(\phi_c) \end{bmatrix} \quad (15)$$

Then equation (15) is solved by an iteration method. The boundary conditions provide the potential $\begin{bmatrix} \phi_a \\ \phi_c \end{bmatrix}$ and the current $\begin{bmatrix} I_a \\ I_c \end{bmatrix} = \begin{bmatrix} f_a(\phi_a) \\ f_c(\phi_c) \end{bmatrix}$. Solution of equation (15) gives $\begin{bmatrix} \phi_a^n \\ \phi_c^n \end{bmatrix}$ at the n^{th} iteration for all metal elements: when

$$\begin{bmatrix} \phi_a^n \\ \phi_c^n \end{bmatrix} - \begin{bmatrix} \phi_a^{n-1} \\ \phi_c^{n-1} \end{bmatrix} \leq \xi \quad (16)$$

where ξ is the tolerance. This provides the calculated values of the potential $\begin{bmatrix} \phi_a^n \\ \phi_c^n \end{bmatrix}$ throughout the boundary. The galvanic current density can be calculated using equations (9) and (10).

2.3 BEASY implementation of BEM

The boundary element program BEASY was used to implement the BEM. The input parameters included the physical geometry of the galvanic couple, the electrolyte conductivity and the boundary conditions of $\begin{bmatrix} \phi_{a0} \\ \phi_{c0} \end{bmatrix}$ and $\begin{bmatrix} f_a'(\phi) \\ f_c'(\phi) \end{bmatrix}$, where ϕ_{a0} was the open circuit potential of the anode; ϕ_{c0} was the open circuit potential of the cathode; $f_a'(\phi)$ was the function used in BEASY to represent the anode metal polarization curve given by equation (9); similarly $f_c'(\phi)$ is the function representing the cathode metal polarization curve. Two methods were used with BEASY to introduce the polarization curve as the boundary condition. These were (1) the linear approach and (2) the piecewise linear approach. For the linear approach $f_a'(\phi)$ and $f_c'(\phi)$ were defined as:

$$f'(\phi) = R_p^{-1}(\phi_{corr} - \phi) = I(\phi) \quad (17)$$

where R_p was the polarization parameter. R_p can be determined for any potential ϕ from the polarization curve as the cotangent of the line connecting ϕ on the polarization curve to the open circuit potential point [8],

$$R_p = \frac{\phi_{corr} - \phi}{I(\phi)}. \quad (18)$$

where ϕ_{corr} is the open circuit potential and $I(\phi)$ is the current density at the potential ϕ. For the linear approach, a particular value of ϕ must be chosen, so that R_p has a constant value. For the piecewise linear approach, the polarization curve was divided into small segments, such that for each segment there was a linear relationship between the potential and current given by:

$$I = f(\phi) = k(\phi - \phi_a) + I_a \quad (19)$$

where k, ϕ_a and I_a were known constants for each line segment.

3 Linear polarization curve

The accuracy of the BEASY program was first evaluated for the one dimension example shown in Fig. 2. The electrolyte was bounded by insulators at x = 0, x = a and z = w. The mesh details are shown in Fig. 3. The boundary of the electrolyte on the surface of the anode and cathode was discretized into 180 elements. *Waber* and *Fagan* [11] have produced an analytical solution and *Aoki* and *Kishimoto* [6] subsequently studied this problem using the BEM approach. The results of *Aoki* and *Kishimoto* [6] were in a good agreement with the analytical solution. The boundary conditions were:

$$I(x, w) = I(0, z) = I(a, z) = 0 \quad (20)$$

$$\phi(x, 0) + R_p I(x, 0) = \phi_a H(x - c) \quad (21)$$

where H represents the Heaviside step function and ϕ_a is a constant equal to 1.0 V. The linear approach and the 50-point piecewise linear approach were utilized in the BEASY program. For the linear approach, the polarization parameter $R_p = |\partial\phi / \partial I|$ was assigned the value of 1.0 for both the anode and cathode. The potential and galvanic current density distributions were calculated using the BEASY program and also using the analytical method [11] along the surface of the galvanic couple for a = 2.0 cm, c/a = 0.5, R_p = 1.0, and w/a was varied from 0.005 to 0.5. The calculated values, Q_a, are presented by the lines in Figs. 4, 6, 8 and 10 and compared with the value, Q_c, of the analytical solution shown by the symbols.

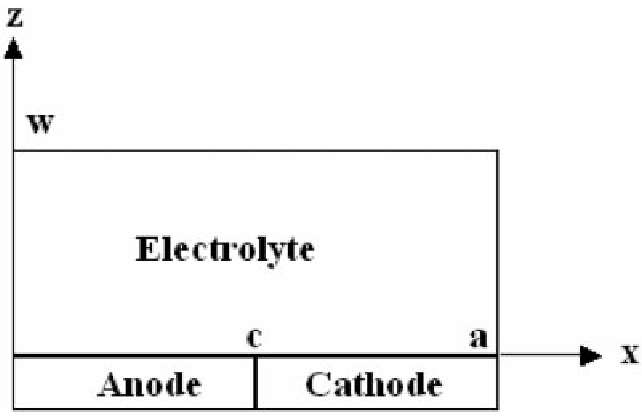

Fig. 2. Definition of the geometry for galvanic corrosion in one-dimension

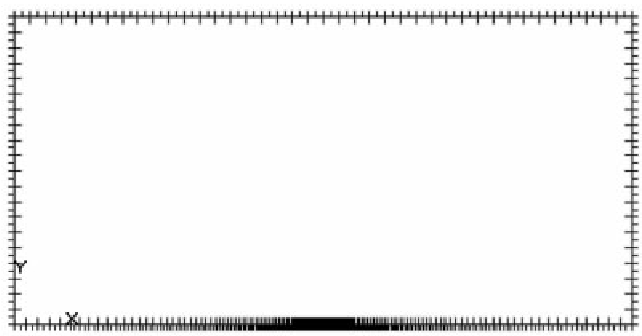

Fig. 3. Schematic illustration of the detail of the BEM mesh for the galvanic corrosion presented in Fig. 2

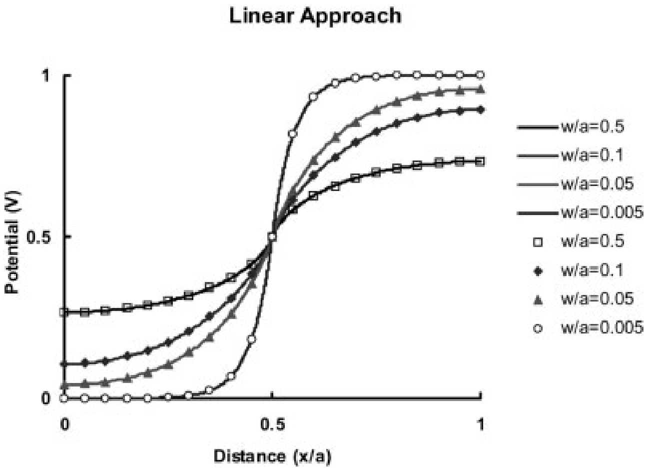

Fig. 4. Calculated values of the potential (full lines) using the linear approach compared with the analytic solution (symbols) for the case of a linear polarization curve

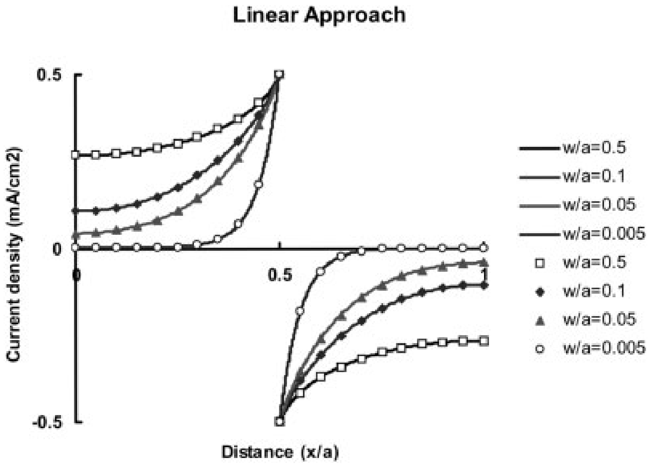

Fig. 6. Calculated values of the current density (full curve) using the linear approach compared with the analytical solution (symbols) for the case of a linear polarization curve

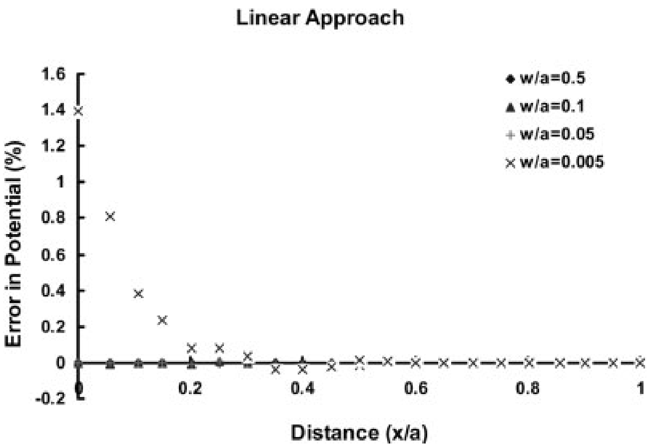

Fig. 5. Error evaluated using equation (22) for the potential calculated using the linear approach and presented in Fig. 4

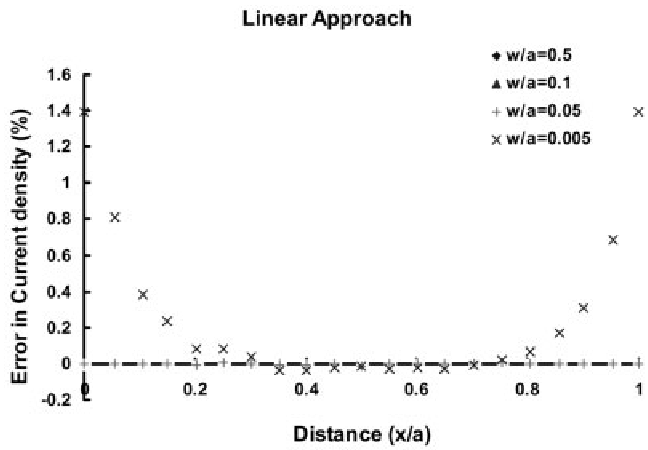

Fig. 7. Error evaluated using equation (22) for the current density calculated using the linear approach and presented in Fig. 6

Figs. 5, 7, 9 and 11 present the error analysis, where the percentage error was calculated from

$$error = \frac{Q_a - Q_c}{Q_a} \times 100\% \qquad (22)$$

For the linear approach, the error in the potential, Fig. 5, and the current density, Fig. 7, were less than 0.2%, except for cases when the calculated and analytic values tended towards zero, but nevertheless, the error was always less than 1.4%. For the 50-point piecewise linear approach, the errors were significantly lower, less than 0.1%.

Further evaluation of the piecewise linear approach was carried out by changing the conductivity of the electrolyte from 0.1 to 10 $\Omega^{-1}\ cm^{-1}$ whilst maintaining the other parameters the same with the constant w/a at 0.05. The potential and galvanic current density distributions calculated by BEASY were compared with the analytical results [3] in Figs. 12–13. The effect of the area ratio of anode/cathode on the potential and current density distributions were also evaluated. The area ratio of anode/cathode was varied from 1:9 to 9:1. The potential and current density distributions cal-

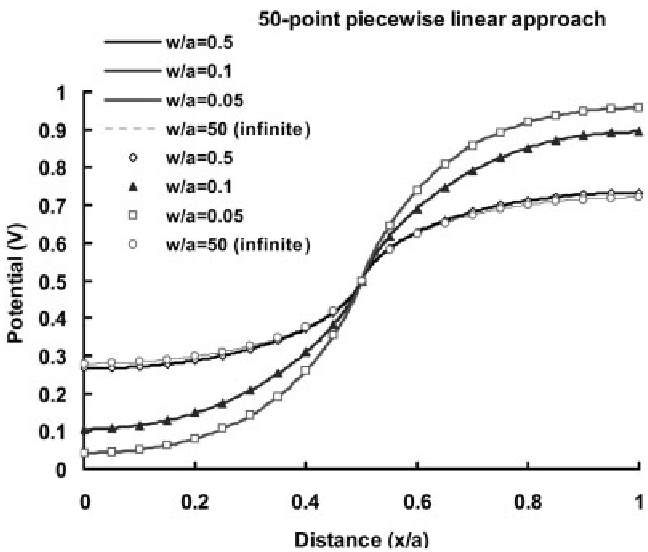

Fig. 8. Calculated values of the potential (full curve) using the 50-point piecewise linear approach compared with the analytical solution (symbols) for the case of a linear polarization curve

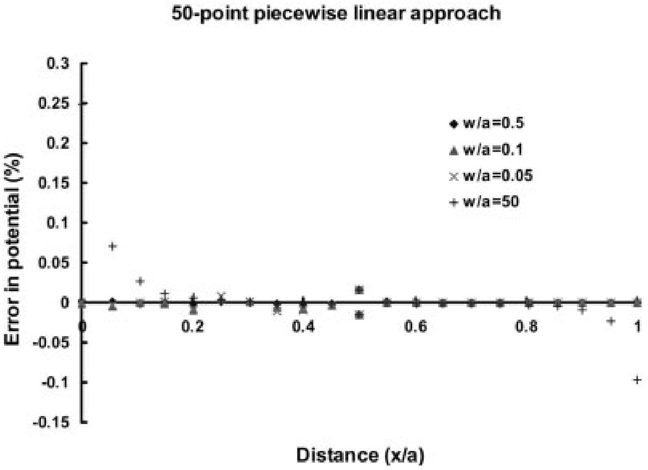

Fig. 9. Error evaluated using equation (22) for the potential calculated using the 50-point piecewise linear approach and presented in Fig. 8

culated from the BEASY program were compared with the analytical results [3] in Figs. 14, 15. It was found that there was good agreement between the values calculated using the 50-point piecewise linear approach and the analytical results.

4 Logarithmic polarization curve

In most circumstances, the boundary conditions as described by equations (9) and (10) are non-linear. In this section, the anode and cathode kinetics were assumed to be given by Tafel equations. The boundary conditions were given by

$$I(x,w) = I(0,z) = I(a,z) = 0 \tag{23}$$

$$I(x,0) = I_{0c}\left\{\exp\left[\frac{(\phi_c - \phi)}{\beta_c}\right] - \exp\left[\frac{(\phi_c - \phi)}{-\alpha_c}\right]\right\}, \text{ for c < x < a,} \tag{24}$$

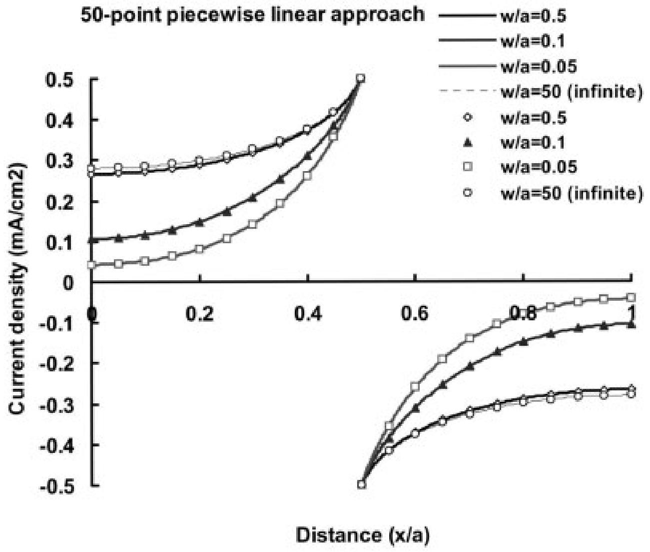

Fig. 10. Calculated values of the current density (full curve) using the 50-point piecewise linear approach compared with the analytical solution (symbols) for the case of a linear polarization curve

$$I(x,0) = I_{0a}\left\{\exp\left[\frac{(\phi_a - \phi)}{\beta_a}\right] - \exp\left[\frac{(\phi_a - \phi)}{-\alpha_a}\right]\right\}, \text{ for 0 < x < c,} \tag{25}$$

where I_{0c}, I_{0a}, ϕ_c, ϕ_a, β_a, β_c, α_c and α_a were given constants. The polarization curves were plotted in Fig. 16 for $\phi_c = -\phi_a = 0.5\ V$, $\alpha_c = \alpha_a = \beta_c = \beta_a = -0.05\ V$, $I_{0c} = I_{0a} = 0.1\ mAcm^{-2}$, $k = 0.1\ \Omega^{-1}cm^{-1}$, where k is the conductivity of the electrolyte.

This case has been investigated by *Doig* and *Flewitt* [12] using the finite difference method. Subsequently, *Aoki* and *Kishmoto* [6] showed that the BEM was in agreement with the prior calculations of *Doig* and *Flewitt*. This case was analysed with the piecewise linear approach using the BEASY program. The values calculated using the BEASY program

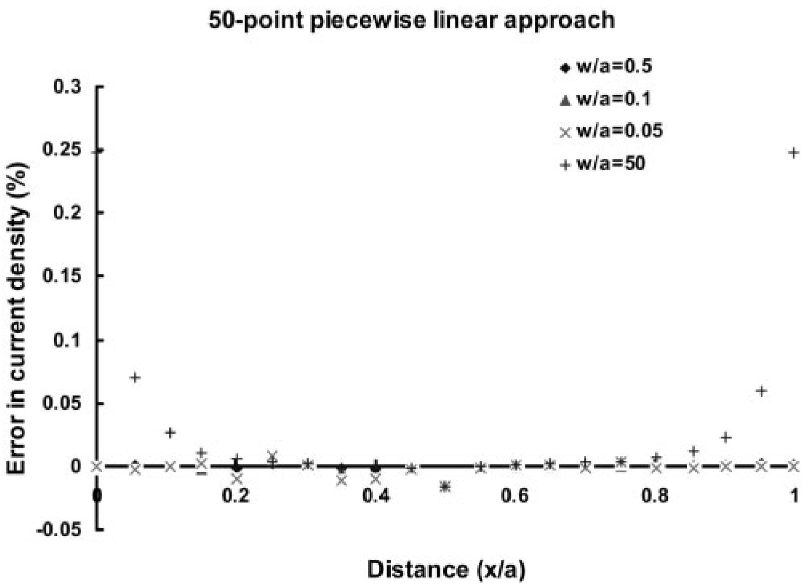

Fig. 11. Error evaluated using equation (22) for the current density calculated using the 50-point piecewise linear approach and presented in Fig. 10

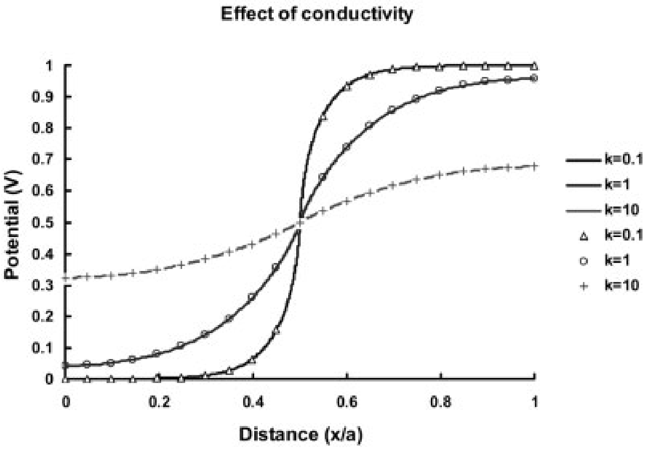

Fig. 12. Calculated values of the potential (full curve) using the 50-point piecewise linear approach compared with the analytical solution (symbols) in solutions of various conductivities for the case of a linear polarization curve

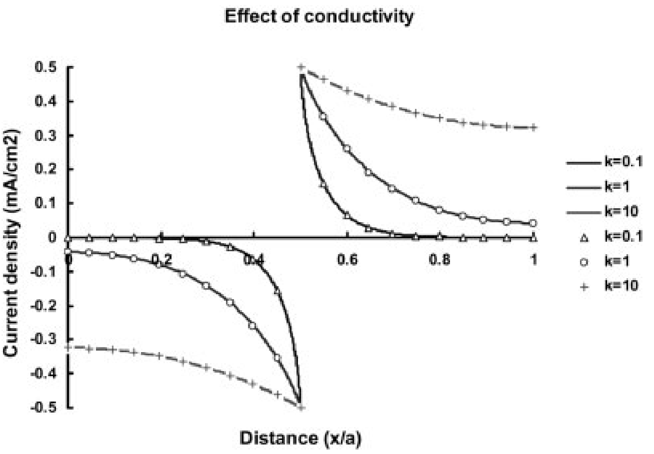

Fig. 13. Calculated values of the current density (full curve) using the 50-point piecewise linear approach compared with the analytical solution (symbols) in solutions of various conductivities for a linear polarization curve

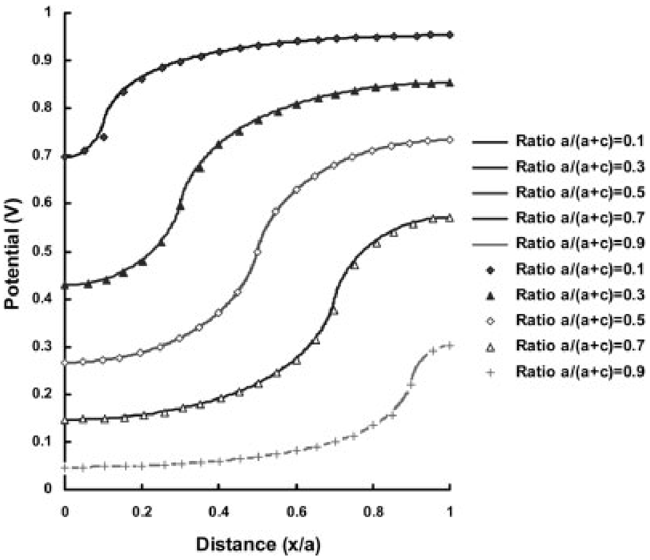

Fig. 14. Calculated values of the potential (full curve) using the 50-point piecewise linear approach compared with the analytical solution (symbols) for various area ratios of the anode/cathode for the case of a linear polarization curve

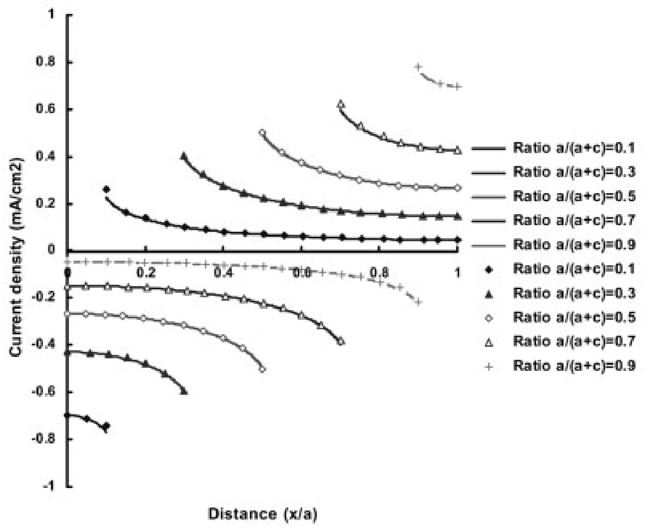

Fig. 15. Calculated values of current density (full curve) using the 50-point piecewise linear approach compared with the analytical solution (symbols) for various area ratios of the anode/cathode for the case of a linear polarization curve

with the 6-point and the 50-point piecewise linear approach are compared with the values from the finite difference method [12] in Figs. 17 and 19, and the error analyses are given in Figs. 18 and 20. The errors were calculated using equation (22). There was good agreement between the BEASY calculations using the piecewise linear approach and the results from the finite difference method. The calculation using the 50-point piecewise linear approach had a better agreement than that using the 6-point piecewise linear approach.

5 Discussion

The BEASY program was extensively evaluated against prior work using the linear approach and the piecewise linear approach to predict potential and galvanic current density distributions for various film thicknesses, various electrolyte conductivities and various area ratios of anode/cathode.

For the linear boundary condition, the calculations using BEASY with the linear approach and the piecewise linear approach gave calculated values in good agreement with the prior results as illustrated in Figs. 4, 6, 8, 10, 12 and 13. The relative error between the BEASY calculated values and the analytical results (shown in Figs. 5, 7, 9 and 11) indicated that there was only a small discrepancy of less than 0.1%, except when the absolute value of the potential and the current density tended to be zero. Nevertheless, the discrepancy was still acceptable as it was less than 1.4%. The distribution of the potential and the current density could also be influenced by the area ratio of anode/cathode. The present modelling results were in good agreement with expectations. The current and potential calculation results were close to the analytical result as illustrated in Figs. 14 and 15.

For logarithmic boundary condition, the 6-point and the 50-point piecewise linear approaches were used in BEASY pro-

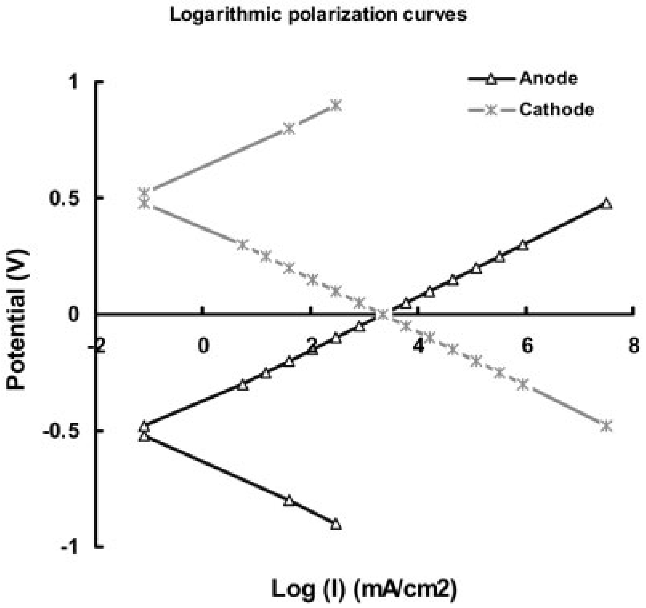

Fig. 16. Logarithmic polarization curves for anode and cathode

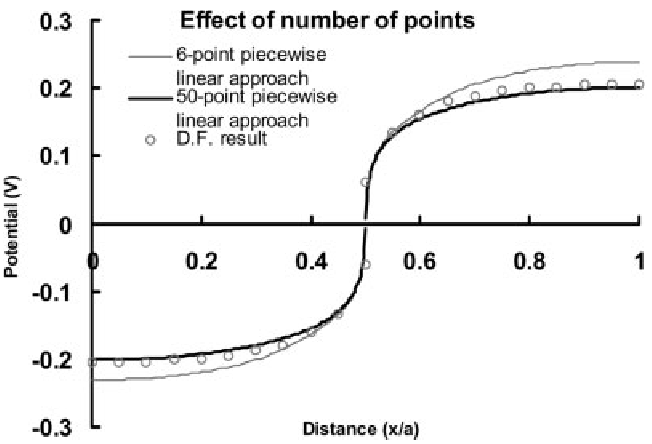

Fig. 17. Calculated values of the potential (full curve) using the 50-point piecewise linear approach compared with the FDM solution (symbols) for the case of a logarithmic polarization curve

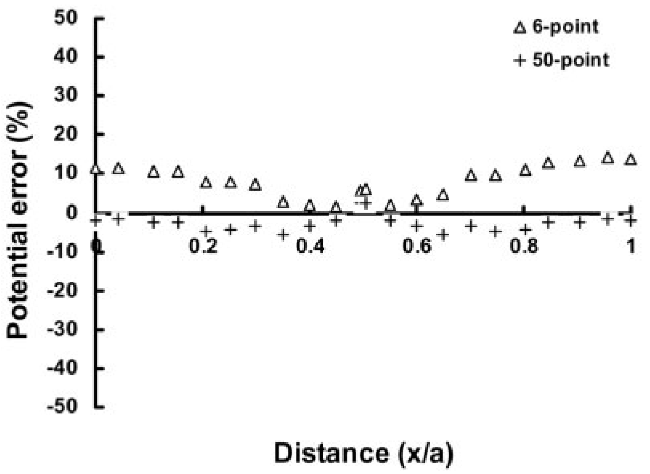

Fig. 18. Potential distribution discrepancy analysis for the results of Fig. 17 using equation (22)

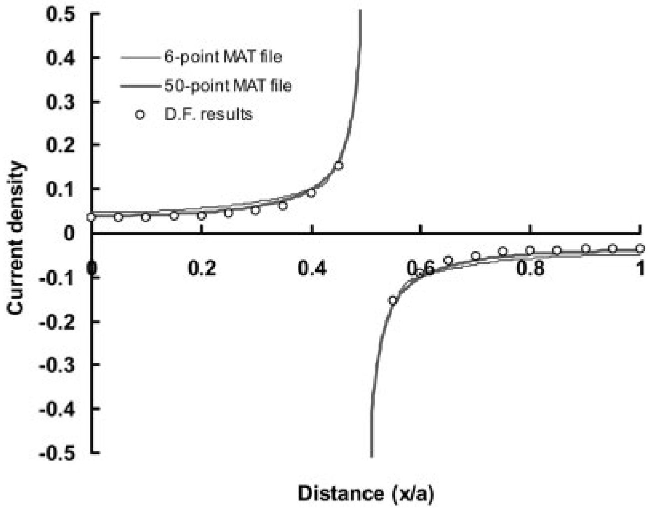

Fig. 19. Calculated values of the current density (full curve) using the 50-point piecewise linear approach compared with the FDM solution (symbols) for the case of a logarithmic polarization curve

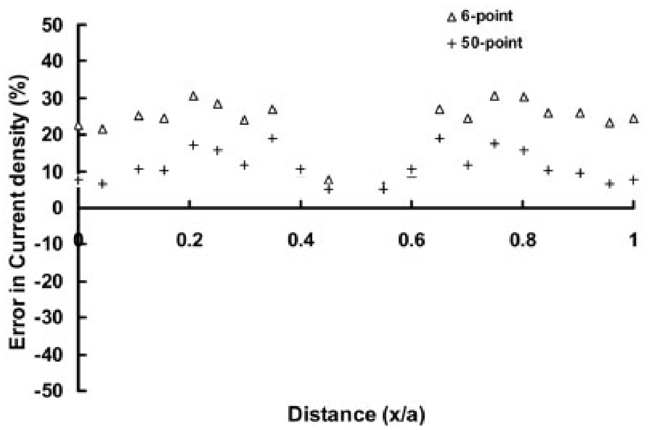

Fig. 20. Current density discrepancy analysis for the results of Fig. 19 using equation (22)

gram. The BEASY modelling results with both of these approaches were in good agreement with the prior results (Figs. 17 and 19) [12]. It was found that the accuracy was in better agreement with the prior result using the 50-point piecewise linear approach than using the 6-point piecewise linear approach.

6 Conclusions

1. The BEASY program using the linear approach and the piecewise linear approach gave accurate predictions of the potential and the galvanic current density distributions for varied electrolyte conditions, various film thicknesses and various electrolyte conductivities for the case of a linear boundary condition.
2. The effect of the area ratio of anode/cathode was also studied. The 50-point piecewise linear approach gave values for the potential and the current density distributions which were in good agreement with the analytical results for the case of a linear boundary condition.

3. The 50-point piecewise linear method could be used with both linear and logarithmic polarization curves.

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