



## Calculation of the oxygen potential profile across solid-state electrochemical cells

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### Abstract

Although several methods of solving the charge and mass transport equations in solid electrolytes wired for device applications have been reported in the literature, there are several inconsistencies. Yuan and Pal have expressed some misgivings regarding the earlier treatment of Choudhury and Patterson. The recent analysis by Näfe is at variance with the analysis of Yuan and Pal. This paper presents a critical examination of various methods for solving transport equations in solid-state electrochemical devices based on mixed ionic-electronic conductors. A complete equivalence between the approaches of Yuan and Pal and Choudhury and Patterson is demonstrated. The oxygen chemical potential profiles generated by both models are identical for a variety of boundary conditions and circuit parameters for a typical cell configuration. The concept of ‘fictitious conductivity’ introduced by Näfe is found to be inappropriate. It implies linear variation of the electrochemical potential of electrons inside the electrolyte, which is not generally valid for a mixed conductor. The oxygen chemical potential profiles inside the electrolyte calculated using Näfe’s equation for different conditions differ substantially from those predicted by the other models. The flawed theoretical formulation is responsible for this mismatch. The methods of Choudhury and Patterson, Riess, and Yuan and Pal are essentially equivalent.

### 1. Introduction

Solution of basic mass and charge transport equations in electrochemical devices employing solid electrolytes with mixed ionic-electronic conduction is the first step in assessing their functional performance characteristics. High-temperature fuel cells, ion pumps, separation membranes and sensors are some of the electrochemical devices of contemporary relevance. There have been numerous approaches in solving the basic transport equations in solid electrolytes with mixed conduction, and in evaluating the effect of mixed conduction on current–voltage and efficiency–voltage relationships in fuel cells. These approaches can be broadly classified into two categories: one employing the equivalent circuit approach pioneered by Takahashi et al. [1] and Tannhauser [2], and the other providing a more general solution of the flux equations [3–7] without the assumption of constant electronic conductivity of the solid electrolyte. The schematic diagrams representing the two approaches are shown in Figures 1 and 2, respectively. The general solution is more rigorous and useful, and is capable of generating the chemical potential profile inside the electrolyte. Yuan and Pal [6] have shown that the average electronic conductivity cannot be treated as constant, if the external load or chemical potential of the mobile ionic species at either electrode changes. Hence, the effect of external load and chemical potentials at the

electrodes on average electronic conductivity must be taken into account while modelling an electrochemical device using the equivalent circuit approach.

Choudhury and Patterson [3] have adopted the basic flux equations for ions and electrons suggested by Wagner [8,9] to an integrable form by capitalizing on various assumptions such as local equilibrium between neutral atoms, ions and electrons, local charge neutrality, virtual stoichiometry, and the Gibbs–Duhem relation. The non-measurable quantities, cation electrochemical potential ( $\eta_1$ ) and anion electrochemical potential ( $\eta_2$ ), were eliminated in favour of the measurable variables oxygen chemical potential ( $\mu_{O_2}$ ) and electrochemical potential of electron ( $\eta_3$ ). The model of Choudhury and Patterson predicts  $\mu_{O_2}$  to be a function of normalized thickness only for constant values of  $r$ , which is defined as the ratio of ionic to electronic current in the solid electrolyte. However, the value of  $r$  is a function of chemical potential at the electrodes, thickness of the electrolyte and the external circuit parameters. The treatment results in implicit equations for the dependence of oxygen potential and current density on the external parameters. The power output and efficiency for a fuel cell based on a mixed conducting solid electrolyte have been calculated as a function of external current.

By assuming that the anion chemical potential ( $\mu_{O^{2-}}$ ) is constant throughout the electrolyte, Riess [4,5] was able

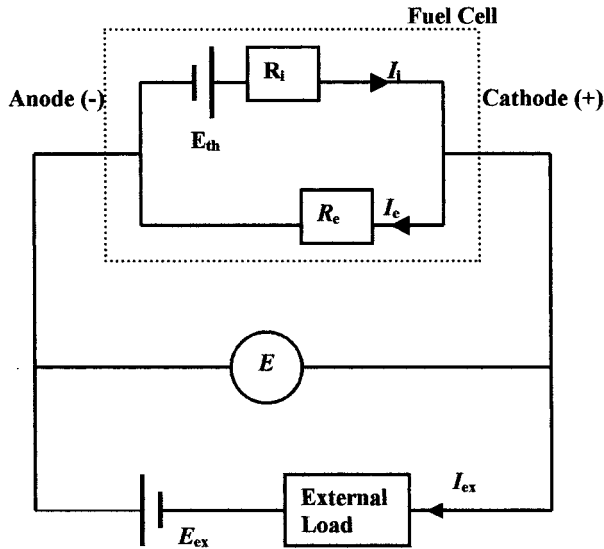


Fig. 1. Equivalent circuit diagram for an electrochemical device such as a fuel cell or an electrochemical pump.

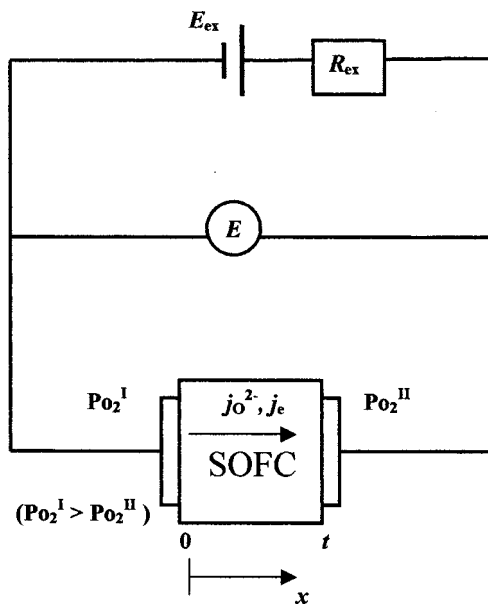


Fig. 2. Schematic of a SOFC connected to a variable external voltage source  $E_{ex}$  and resistance  $R_{ex}$ .

to solve the electronic and ionic current flux equations in a relatively simple manner. Solution of the electronic flux equation gives electron or hole concentration as a function of terminal voltage, electronic current density and properties of the electrolyte. The electronic current density is determined by applying boundary conditions. Since oxygen chemical potential is related to the electron or hole concentration, it is possible to calculate the oxygen chemical potential profile inside the electrolyte from the variation of electron or hole concentration with distance. The approaches of Riess [4,5] and Choudhury and Patterson [3] have been shown to be virtually equivalent by Näge [10]. Although there are differences in the course of derivation, both approaches

yield essentially the same final results. However, the approach by Choudhury and Patterson [3] seems to be less restrictive since formulation of the theory does not involve the assumption of constant chemical potential of mobile ions ( $\mu_{O^{2-}}$ ), although the assumption is used in their paper to simplify the solution. By contrast, the Riess model [4, 5] relies on this assumption from the beginning to develop the theory, which is valid for doped solid electrolytes in which extrinsic vacancies are much greater than intrinsic defects.

Considering only anions to be mobile, Yuan and Pal [6] derived integral equations for ionic and electronic current flux through a multielectrolyte assembly connected to an external voltage source and a resistance. The effect of external voltage and resistance on cell performance can be evaluated using their analysis. The treatment can generate oxygen chemical potential at each interface and chemical potential profile inside each layer. This allows tailoring of electrolyte layer thickness in order to optimize transport properties and ensure chemical stabilities of interfaces. However, the assumption that only anions are mobile makes this model less generic than that of Choudhury and Patterson, which also takes into account cationic mobility. Although Yuan and Pal [6] did not compare their model predictions for single layer structure with those of Choudhury and Patterson [3] or Riess [4, 5], the authors suggest a major difference in the oxygen potential profile in the electrolyte under load.

More recently Näge [7] has disputed the oxygen potential profile generated by the analysis of Yuan and Pal [6]. Differences in the oxygen potential profile inside the electrolyte can lead to disharmony between other relationships such as current–voltage or efficiency–voltage. The purpose of this communication is to examine critically the models reported in the literature and to identify sources of discrepancies.

## 2. Basic equations

Consider an oxide solid electrolyte of linear geometry characterized by unidirectional flux of charged species. For simplicity, anions are assumed to be the only mobile ionic species. Local current density associated with a charged species  $k$  is given by

$$j_k = -\frac{\sigma_k}{z_k F} \text{grad}(\eta_k) \quad (1)$$

where,  $j_k$ ,  $\sigma_k$ ,  $\eta_k$  and  $z_k$  are the current density, conductivity, electrochemical potential and valency of species  $k$  in the electrolyte and  $F$  is the faradaic constant. The electrochemical potential  $\eta_k$  of the charged species is defined by

$$\eta_k = \mu_k + z_k F \phi_k \quad (2)$$

where  $\phi$  is the electric potential and  $\mu_k$  is the chemical potential of species  $k$ .

From Equations 1 and 2 the current flux equations for oxygen anions and electrons may be written as

$$j_{O^{2-}} = \frac{\sigma_{O^{2-}}}{2F} \left[ \frac{d\mu_{O^{2-}}}{dx} - 2F \frac{d\phi}{dx} \right] \quad (3)$$

$$j_e = \frac{\sigma_e}{F} \left[ \frac{d\eta_e}{dx} \right] = \frac{\sigma_e}{F} \left[ \frac{d\mu_e}{dx} - F \frac{d\phi}{dx} \right] \quad (4)$$

External current in the circuit shown in Figure 2 is given as

$$j_{ex} = j_{O^{2-}} + j_e = \frac{I_{ex}}{A} \quad (5)$$

where  $I_{ex}$  and  $j_{ex}$  are the external current and current density, respectively, and  $A$  is the cross-sectional area of the electrolyte. At steady state both ionic and electronic currents in the electrolyte are constant. If any of these were to vary with  $x$ , then a build-up or depletion of anions or electrons at some point in the crystal would result, contrary to the steady-state assumption.

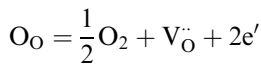
If it is assumed that the electrodes are reversible and the electrochemical potential of electrons at each electrolyte surface equals that at electrode in contact with the electrolyte, then the terminal voltage is given by

$$\eta_e'' - \eta_e' = -FE \quad (6)$$

From Figure 2 it is seen that the external current is related to the difference between externally applied voltage  $E_{ex}$  and terminal voltage  $E$ , and the external resistance  $R_{ex}$  according to Equation 7:

$$I_{ex} = \frac{E - E_{ex}}{R_{ex}} \quad (7)$$

The equilibrium between oxygen gas molecules ( $O_2$ ), oxygen ions on regular lattice sites ( $O_O$ ), oxygen vacancies ( $V_O$ ) and electrons can be represented as:



following the Kröger–Vink notation. The electron concentration ( $n$ ) at any location in the electrolyte is then related to the oxygen partial pressure ( $P_{O_2}$ ) as follows:

$$n = \left( \frac{K}{V_O} \right) P_{O_2}^{-1/4} \quad (8)$$

where  $K$  is the equilibrium constant for the reaction. The fundamental equations listed above are undisputed in the literature.

### 3. Incorrect formulation of Nāfe

To describe the external current density ( $j_{ex}$ ) in a way corresponding to Equation 1, Nāfe introduced the

concept of ‘fictitious conductivity’,  $\sigma_{ext}$ , defined as the ratio of the external current density to electric field strength that would cause this current flux to flow through the electrolyte:

$$\sigma_{ext} = \frac{-(I_{ex}/A)}{(E/t)} = \frac{t[1 - (E_{ex}/E)]}{R_{ex}A} \quad (9)$$

where  $t$  is the thickness of the electrolyte, and field strength is represented by the ratio of terminal voltage to electrolyte thickness.

Using Equation 9, Nāfe formulated the external current density as an apparent electron current density of the electrolyte with the same driving force as the internal electron current density  $j_e$ :

$$j_{ex} = \frac{t[1 - (E_{ex}/E)]}{R_{ex}AF} \text{grad}(\eta_e) \quad (10)$$

A direct comparison of Equations 9 and 10 leads to the following relation:

$$\text{grad}(\eta_e) = -F \left( \frac{E}{t} \right) \quad (11)$$

This implies that  $\text{grad}(\eta_e)$  is constant throughout electrolyte for a given value of terminal voltage  $E$ . The electrochemical potential of electron is then constrained to vary linearly inside the electrolyte. Such a behaviour is expected in metals and semiconductors but is not generally valid for a solid electrolyte with mixed ionic and electronic conduction. Further, constancy of internal electronic current under steady-state condition demands that both electronic conductivity and  $\text{grad}(\eta_e)$  are constant, or both vary in such a manner that their product remains constant as suggested by Equation 1. From Equation 8, it follows that electron concentration is function of oxygen partial pressure and varies with distance  $x$  inside the electrolyte. Since electron concentration and hence electronic conductivity inside electrolyte varies with distance  $x$  under the steady-state condition, it is not possible for  $\text{grad}(\eta_e)$  to be a constant as implied by Equation 11. Hence, the formulation of the concept of ‘fictitious conductivity’,  $\sigma_{ext}$ , by Nāfe is basically unsound and can lead to distortions in the predicted cell characteristics.

For comparing the oxygen chemical potential profile generated using the models of Choudhury and Patterson [3], Yuan and Pal [6] and Nāfe, calculations are performed for a typical cell incorporating a ceria-based electrolyte. Since the models of Choudhury and Patterson [3] and Riess [4, 5] has been shown analytically to yield the same result [10], calculations using the Riess model are not performed to avoid redundancy. The circuit and electrolyte parameters used in the calculation are the same as those chosen by Nāfe [7]. Five different combinations of electrolyte thickness ( $t$ ) and external voltage ( $E_{ex}$ ) are chosen; (a)  $t = 100 \mu\text{m}$  and  $E_{ex} = -0.5 \text{ V}$ , (b)  $t = 100 \mu\text{m}$  and  $E_{ex} = 0 \text{ V}$ , (c)  $t = 100 \mu\text{m}$

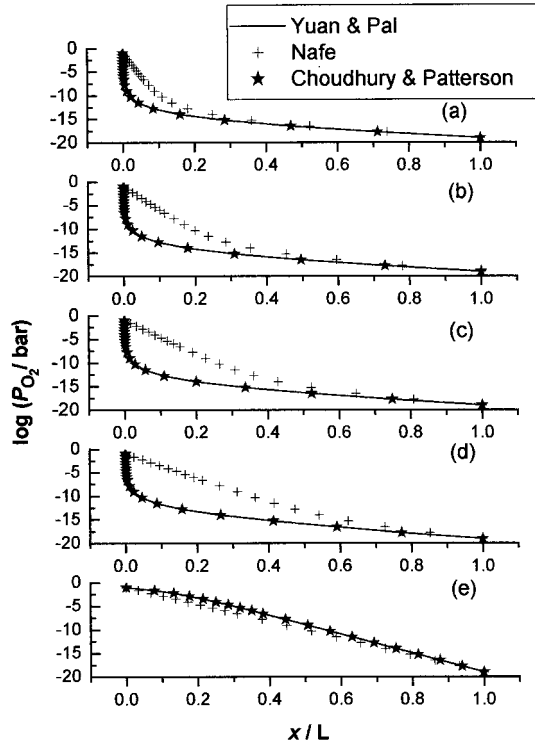


Fig. 3. Comparison of oxygen chemical potential profiles through a typical ceria-based solid electrolyte calculated using the models by Choudhury and Patterson [3], Yuan and Pal [6] and Näfe [7] for different imposed conditions: (a)  $t = 100 \mu\text{m}$ ,  $E_{\text{ex}} = -0.5 \text{ V}$ , (b)  $t = 100 \mu\text{m}$ ,  $E_{\text{ex}} = 0 \text{ V}$ , (c)  $t = 100 \mu\text{m}$ ,  $E_{\text{ex}} = 0.5 \text{ V}$ , (d)  $t = 200 \mu\text{m}$ ,  $E_{\text{ex}} = 0.5 \text{ V}$  and (e)  $t = 200 \mu\text{m}$ ,  $E_{\text{ex}} = 6 \text{ V}$ .

and  $E_{\text{ex}} = 0.5 \text{ V}$ , (d)  $t = 200 \mu\text{m}$  and  $E_{\text{ex}} = 0.5 \text{ V}$ , and (e)  $t = 200 \mu\text{m}$  and  $E_{\text{ex}} = 6 \text{ V}$ . The external resistance, temperature, oxygen partial pressure at the electrodes and cross-sectional area of the electrolyte are kept constant;  $R_{\text{ex}} = 1 \Omega$ ,  $T = 1173 \text{ K}$ ,  $P'_{\text{O}_2} = 0.101325 \text{ bar}$ ,  $P''_{\text{O}_2} = 1.01325 \times 10^{-19} \text{ bar}$ ,  $A = 1 \text{ cm}^2$ . The partial ionic and electronic conductivities of the solid electrolyte used in the calculations are  $\sigma_{\text{O}^{2-}} = 0.1 \text{ S cm}^{-1}$  and  $\sigma_e = 10^{-5} (P_{\text{O}_2})^{-1/4} \text{ S cm}^{-1}$ , respectively. These correspond to values for  $\text{CeO}_2\text{-5 mol \% Y}_2\text{O}_3$  at  $1173 \text{ K}$ . Under these conditions, the open circuit emf ( $E_{\text{OC}}$ ) of the cell calculated using the relation:

$$E_{\text{OC}} = \frac{RT}{nF} \int t_{\text{O}^{2-}} d \ln(P_{\text{O}_2})$$

is  $-0.9607 \text{ V}$ . In the expression above,  $R$  is the universal gas constant and  $T$  the absolute temperature, and  $t_{\text{O}^{2-}}$  the transport number of oxygen ions defined as the fraction of total current carried by oxygen ions when no

chemical potential gradients prevail. The calculated oxygen chemical potential profiles are shown in Figure 3. It is clear that the oxygen chemical potential profiles calculated using the model of Choudhury and Patterson are coincident with the curves generated by the model of Yuan and Pal for all the five cases. The profiles obtained using the Näfe model deviate dramatically from the others, especially near the high oxygen potential electrode. The terminal voltage  $E$  calculated using the different approaches for the five cases are listed in Table 1. The oxygen potential profile through the solid electrolyte approaches linearity as the terminal voltage approaches zero. The results generated by the Näfe treatment are again significantly different from that obtained using the models of Choudhury and Patterson and Yuan and Pal. This discrepancy arises from the wrong conceptual formulation of 'fictitious conductivity',  $\sigma_{\text{ext}}$ . Thus, the equations developed by Näfe [7] cannot be considered as generalized versions of the Wagner-Schmalzried equations.

#### 4. Comparison of analyses: Yuan and Pal vs Choudhury and Patterson

Yuan and Pal [6] assumed local equilibrium to prevail between diatomic oxygen in the gas phase, and oxygen ions and electrons in the solid electrolyte at each electrolyte-gas interface:



The chemical potentials of the three species are then related:

$$\mu_{\text{O}^{2-}} = \frac{1}{2} \mu_{\text{O}_2} + 2\mu_e \quad (13)$$

By definition, the oxygen potential is connected to the oxygen partial pressure in the gas phase,

$$\mu_{\text{O}_2} = \mu_{\text{O}_2}^\circ + RT \ln(P_{\text{O}_2}) \quad (14)$$

where  $\mu_{\text{O}_2}^\circ$  is the chemical potential of oxygen in its standard state.

By combining Equations 2, 3 and 13,

$$j_{\text{O}^{2-}} = \frac{\sigma_{\text{O}^{2-}}}{4F} \left[ \frac{d\mu_{\text{O}_2}}{dx} + 4 \frac{d\eta_e}{dx} \right] \quad (15)$$

Table 1. Cell terminal voltage  $E$  calculated using models of Choudhury and Patterson, Yuan and Pal, and Näfe for five different operating conditions depicted in Figure 3

Model	Terminal voltage/V				
	(a)	(b)	(c)	(d)	(e)
Choudhury and Patterson [3]	-0.8406	-0.8174	-0.7929	-0.7248	0.1269
Yuan and Pal [6]	-0.8406	-0.8175	-0.7927	-0.7251	0.1279
Näfe [7]	-0.8269	-0.7858	-0.7450	-0.6514	0.0

From Equations 4 and 15, one obtains

$$\frac{j_{O^{2-}}}{\sigma_{O^{2-}}} - \frac{j_e}{\sigma_e} = \frac{1}{4F} \frac{d\mu_{O_2}}{dx} \quad (16)$$

With the help of Equations 5 and 16, the expression for external current density ( $j_{ex}$ ) may be written as

$$\left( \frac{j_{ex}}{1 + \left(\frac{j_{O^{2-}}}{j_e}\right)} \right) \left( \frac{\sigma_e \left(\frac{j_{O^{2-}}}{j_e}\right) - \sigma_{O^{2-}}}{\sigma_e \sigma_{O^{2-}}} \right) = \frac{1}{4F} \frac{d\mu_{O_2}}{dx} \quad (17)$$

At steady state, the fluxes  $j_e$  and  $j_{O^{2-}}$  will be constant and, therefore, their ratio ( $j_{O^{2-}}/j_e$ ), which is defined as parameter  $r$  by Choudhury and Patterson, will also be a constant. Equation 17 can be integrated to give

$$j_{ex}t = \int_{\mu'_{O_2}}^{\mu''_{O_2}} \frac{(1+r)\sigma_e\sigma_{O^{2-}}}{r\sigma_e - \sigma_{O^{2-}}} \left( \frac{1}{4F} \right) d\mu_{O_2}$$

The external current is given by

$$I_{ex} = \frac{A}{t} \int_{\mu'_{O_2}}^{\mu''_{O_2}} \frac{(1+r)\sigma_e\sigma_{O^{2-}}}{r\sigma_e - \sigma_{O^{2-}}} \left( \frac{1}{4F} \right) d\mu_{O_2} \quad (18)$$

The oxygen ion conductivity ( $\sigma_{O^{2-}}$ ) is constant at a given temperature for a material in which the concentration oxygen vacancies is set by the dopant. The dependence of  $\sigma_e$  on  $\mu_{O_2}$  or  $P_{O_2}$  can be deduced from Equation 8. Thus, Equation 18 can be integrated between specified limits to obtain the value of external current for a given value of  $r$ . This equation is identical to that derived by Choudhury and Patterson [3]. In a similar fashion, equivalent expressions for terminal voltage and potential profile inside electrolyte can be derived using Yuan and Pal approach [6] and shown to be the same as that arrived by Choudhury and Patterson [3].

Incorporation of an additional relationship that follows from either Figure 1 or 2,

$$I_{ex} = \frac{E - E_{ex}}{R_{ex}} = \frac{\frac{\eta'' - \eta'}{(-F)} - E_{ex}}{R_{ex}} \quad (19)$$

into Choudhury and Patterson model [3], leads to the final expression for ionic current flux equivalent to that by Yuan and Pal [6]. According to Choudhury and Patterson [3], current flux densities due to oxygen ions and electrons are given by

$$j_{O^{2-}} = \sigma_{O^{2-}} \left( \frac{1}{4F} \text{grad}(\mu_{O_2}) + \frac{1}{F} \text{grad}(\eta_e) \right)$$

and

$$j_e = \frac{\sigma_e}{F} \text{grad}(\eta_e)$$

For comparison with the equations of Yuan and Pal [6], the oxygen and electron fluxes in the electrolyte can

be rewritten in units of equivalents per unit area per unit time,  $J_{O^{2-}}$  and  $J_e$ . Thus,

$$J_{O^{2-}} = \left( -\frac{j_{O^{2-}}}{F} \right) = -\frac{\sigma_{O^{2-}}}{4F^2} \frac{d\mu_{O_2}}{dx} - \frac{\sigma_{O^{2-}}}{F^2} \frac{d\eta_e}{dx} \quad (20)$$

$$J_e = \left( -\frac{j_e}{F} \right) = -\frac{\sigma_e}{F^2} \frac{d\eta_e}{dx} \quad (21)$$

The external current can be expressed in terms of the fluxes of electrons and ions in the electrolyte. Thus,

$$I_{ex} = A(j_e + j_{O^{2-}}) = -FA(J_e + J_{O^{2-}}) \quad (22)$$

From Equations 20 and 21, one obtains

$$\frac{J_{O^{2-}}}{\sigma_{O^{2-}}} - \frac{J_e}{\sigma_e} = \frac{-1}{4F^2} \frac{d\mu_{O_2}}{dx} \quad (23)$$

Integration of Equation 20, under steady state condition gives

$$J_{O^{2-}}t = \frac{RT\sigma_{O^{2-}}}{4F^2} \ln \frac{P'_{O_2}}{P''_{O_2}} - \frac{\sigma_{O^{2-}}}{F^2} (\eta'' - \eta') \quad (24)$$

Utilizing Equations 19, 22, 23 and 24 to eliminate ( $\eta'' - \eta'$ ),  $I_{ex}$ , and  $J_e$ , gives

$$J_{O^{2-}} = \frac{1}{1 + \frac{t}{R_{ex}A(\sigma_e + \sigma_{O^{2-}})}} \left[ \frac{E_{ex}\sigma_{O^{2-}}}{FAR_{ex}(\sigma_e + \sigma_{O^{2-}})} + \frac{RT\sigma_{O^{2-}} \ln \left( \frac{P'_{O_2}}{P''_{O_2}} \right)}{4F^2 AR_{ex}(\sigma_e + \sigma_{O^{2-}})} - \frac{1}{4F^2} \frac{\sigma_e\sigma_{O^{2-}}}{\sigma_e + \sigma_{O^{2-}}} \frac{d\mu_{O_2}}{dx} \right] \quad (25)$$

This is the same general equation generated by Yuan and Pal [6] to calculate oxygen ion flux  $J_{O^{2-}}$ . Yuan and Pal [6] have given an analytical solution of this equation.

Thus, it can be concluded that approaches by Choudhury and Patterson [3] and Yuan and Pal [6] are essentially equivalent. Hence, there should be no difference in oxygen chemical potential profile predicted by them, contrary to the claim by Yuan and Pal [6]. The equivalence of the two approaches can be further demonstrated by numerical computation.

For comparison of the predictions of the two models, calculated oxygen chemical potential profiles for the typical ceria-based electrolyte are shown in Figure 4. Four different combinations of electrolyte thickness ( $t$ ) and external voltage ( $E_{ex}$ ) selected earlier by Yuan and Pal [6] are used; (a)  $t = 200 \mu\text{m}$  and  $E_{ex} = 3 \text{ V}$ , (b)  $t = 100 \mu\text{m}$  and  $E_{ex} = 3 \text{ V}$ , (c)  $t = 200 \mu\text{m}$  and  $E_{ex} = 6 \text{ V}$  and (d)  $t = 100 \mu\text{m}$  and  $E_{ex} = 6 \text{ V}$ . The cell is in charging mode in all four cases. All other input parameters and electrolyte properties used in the calculation are the same as those specified for Figure 3. It is

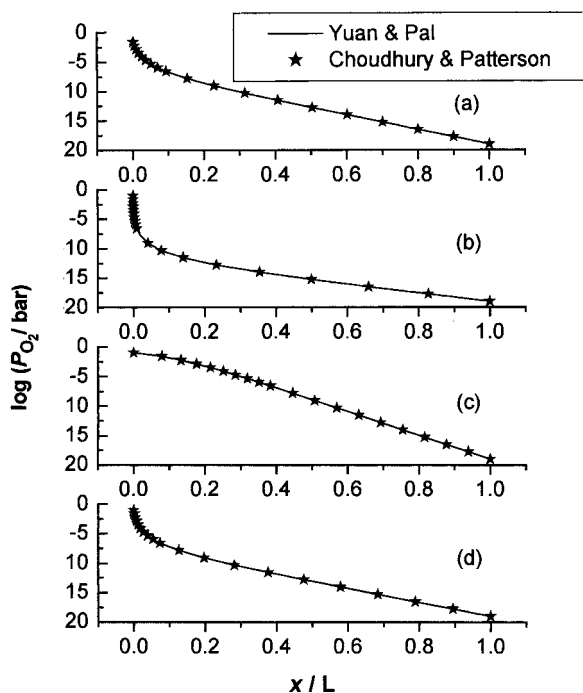


Fig. 4. Comparison of oxygen chemical potential profiles through a typical ceria-based solid electrolyte calculated using the models by Choudhury and Patterson [3] and Yuan and Pal [6] under the specified conditions: (a)  $t = 200 \mu\text{m}$ ,  $E_{\text{ex}} = 3 \text{ V}$ , (b)  $t = 100 \mu\text{m}$ ,  $E_{\text{ex}} = 3 \text{ V}$ , (c)  $t = 200 \mu\text{m}$ ,  $E_{\text{ex}} = 6 \text{ V}$  and (d)  $t = 100 \mu\text{m}$ ,  $E_{\text{ex}} = 6 \text{ V}$ .

clear from the Figure 4 that both of the approaches predict the same oxygen potential profile for all cases. The terminal voltage  $E$  calculated using the two models for the four cases listed above are also the same as shown in Table 2. Small differences, less than 2 mV, are caused by errors in integration. The oxygen potential profiles displayed in Figure 3, where different combinations of electrolyte thickness and external voltage and oxygen partial pressures at the electrodes are specified, also confirm this conclusion.

Hence, the earlier assertion by Yuan and Pal [6] that the Choudhury and Patterson model [3] predicts the oxygen chemical potential profile to be only a function of normalized thickness and does not take into account the thickness variation of the electrolyte is misleading. Perhaps, they overlooked the fact that the equations of Choudhury and Patterson [3] apply only at constant values of  $r$ . A change in thickness of the electrolyte alters both ionic and electronic currents in the material, and hence the value of  $r$ .

Table 2. Cell terminal voltage  $E$  calculated using models of Choudhury and Patterson, and Yuan and Pal for four different operating conditions depicted in Figure 4

Model	Terminal voltage /V			
	(a)	(b)	(c)	(d)
Choudhury and Patterson [3]	-0.3688	-0.6396	0.1269	-0.4012
Yuan and Pal [6]	-0.3681	-0.6421	0.1279	-0.4018

## 5. Summary

A critical review of published models for calculating chemical potential variation, current-voltage characteristics, charge distribution and efficiency of solid state devices incorporating mixed ionic-electronic conductors, indicates the analysis of Choudhury and Patterson [3], Riess [4,5] and Yuan and Pal [6] are essentially equivalent. They are developed from the classical approach of Wagner [8,9] for the open circuit case. The misgivings expressed by Yuan and Pal [6] about the earlier treatment of Choudhury and Patterson [3] is invalid. The recent formulation of Näfe [7] for solving the transport equations in solid electrolytes is incorrect. The device characteristics calculated using Näfe's model [7] do not match those generated by the other models [3-6]. The problem is associated with the introduction of the concept of 'fictitious conductivity',  $\sigma_{\text{ext}}$ , by Näfe in order to describe the current in the external circuit in a manner similar to charge flux in the solid electrolyte.

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