NASA Aerospace Battery Workshop

Solid-state electrochemical transport theory

Xinfang Jin

2016 Fall

Outline

- ❖ Charge Transport in MIECs-Literature Review

- ❖ MATHEMATICAL MODELS
  - Nernst-Planck Theory.

  Focus: Application in MIEC electrode/electrolyte (governing equations and boundary conditions).
  - Modified Fick's diffusion equation.

  Focus: Derivation procedures.

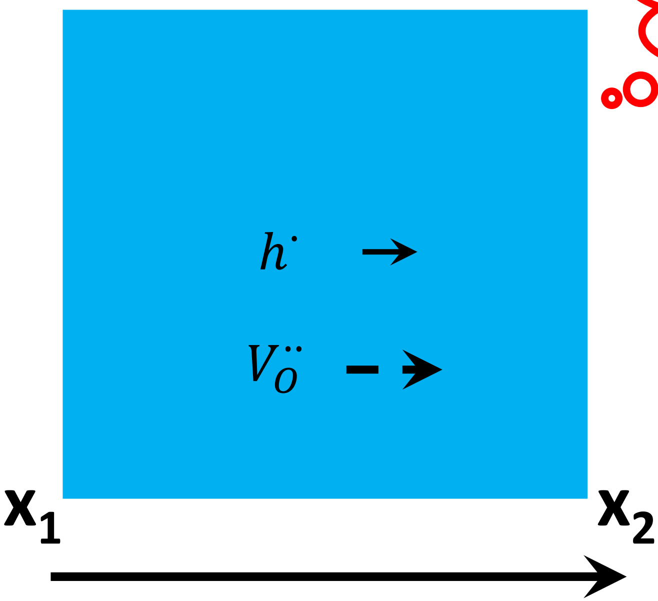
  Relationship with Nernst-Planck Theory.

  Application in MIEC electrode.

- ❖ SUMMARY AND FUTURE WORK

Charge Transport in MIEC

MIEC



What is the driving Force for the transport of charged species?

Concentration Gradient

Electric potential Gradient

$$\nabla \mu_j = R_g T \nabla \ln c_j + z_j F \nabla \phi$$

Electrochemical potential gradient

$$\mathbf{N_j} = -AD_j \nabla c_j$$

Modified Fick's diffusion equation

$$\mathbf{N_j} = -D_j \nabla c_j - \frac{c_j z_j F D_j}{R_g T} \nabla \phi$$

Nernst-Planck

Literature Review-Experimental techniques

Transient Phenomena

ECR

Abrupt change of PO_2 under fixed T

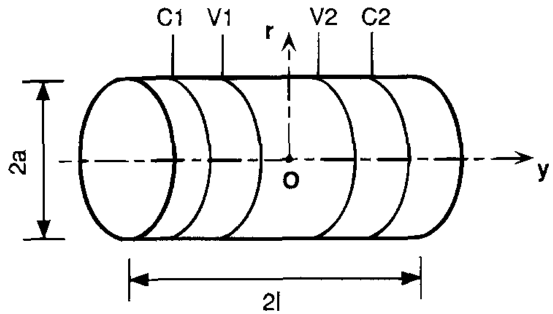
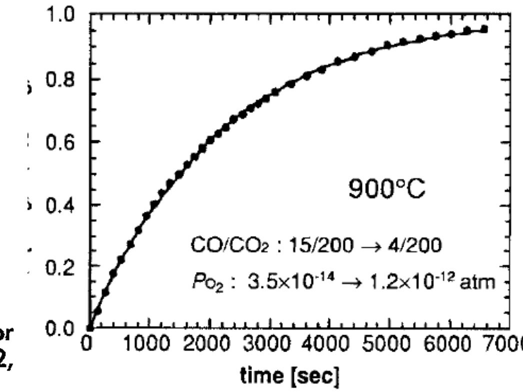


Fig. 1. The geometry of the specimen and the coordination for mathematical treatments (C1 and C2, current leads; V1 and V2, voltage probes).



J. Electrochern. Soc., Vol. 141, No. 5, May 1994

EIS

AC voltage
AC current

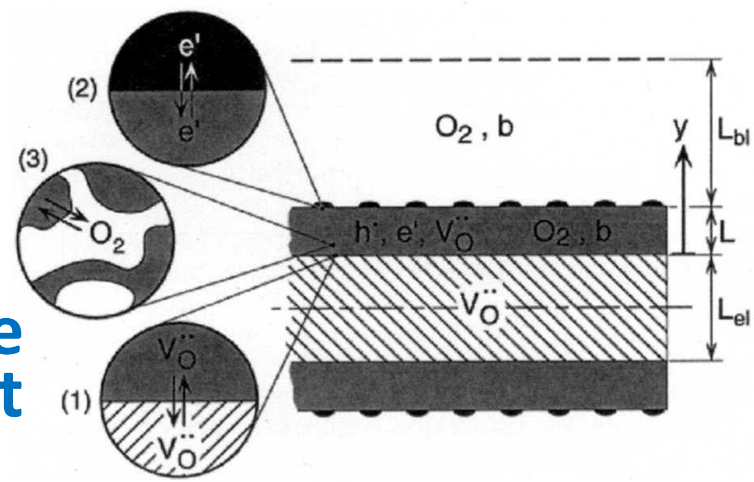
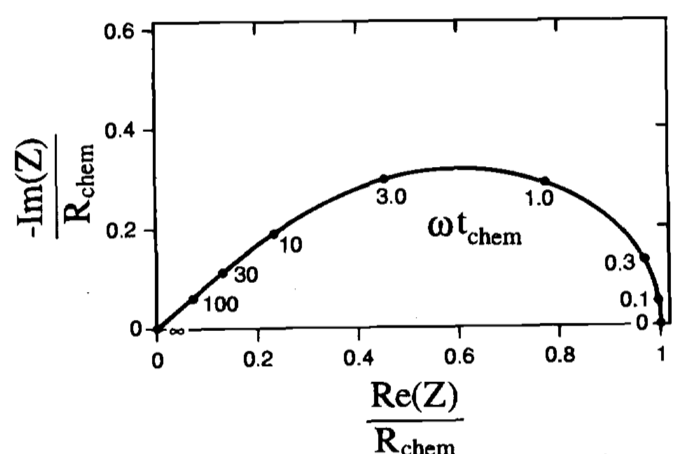


Fig. 3. Cell geometry considered in the model, and as explained in the text.



J. Electrochem. Soc., Vol. 143, No. 11, Nov. 1996

Literature Review-Modeling of MIEC

Modified Fick's diffusion equation

Carl Wagner

Mixed conduction Li_3Sb system

Weppner and Huggins,1977

$$N_j = -D_j W \frac{\partial c_j}{\partial x}$$

Enhancement Factor

$$W = t_e \left[\frac{\partial \ln a_j}{\partial \ln c_j} + z_j \frac{\partial \ln a_e}{\partial \ln c_j} \right] \overset{\gamma_j, \gamma_e = cons\tan t}{=} t_e \left[1 + z_j^{\ 2} \frac{c_j}{c_e} \right]$$

Mixed conduction in both solid and liquid

Schmalzried,1981

Thermodynamic Factor

$$A = \left[1 + \left(\frac{\partial \ln \gamma_j}{\partial \ln c_j} \right) \right] \qquad D_j = D_j A$$

Mixed conduction in both solid solution Bouwmeester 1997, Adler 1996

$$A = \frac{1}{RT} \frac{\partial \mu_O}{\partial \ln c_O} = \frac{1}{RT} \frac{\partial \left(\mu_O^{\ 0} + RT \ln \sqrt{p_{O_2}} \right)}{\partial \ln c_O} = \frac{1}{2} \frac{\partial \ln p_{O_2}}{\partial \ln c_O}$$

$$A = -\frac{1}{2} \frac{\partial \ln p_{O_2}}{\partial \ln c_v} = 1 + \frac{\partial \ln f_{j,e}}{\partial \ln c_v} + \frac{\partial \ln c_e^{\ 2}}{\partial \ln c_v}$$

Literature Review-Modeling of MIEC

Nernst-Planck

$$\mathbf{N_j} = -D_j \nabla c_j - \frac{c_j z_j F D_j}{R_g T} \nabla \phi$$

Charge transport of MIEC thin-film electrode
Liu,2007-2010

Questioned Fermi Level assumption in Adler's model
Liu and Winnick, 1997

Voltage-current relationship for MIEC electrolyte Wachsman and Duncan, 2009

Impedance model for MIEC electrolyte Haile and Goodwin, 2005-2011

Research Goals

Modified Fick's law **VS** **Nernst-Planck**

Fermi Level Assumption?

Thermodynamic factor?

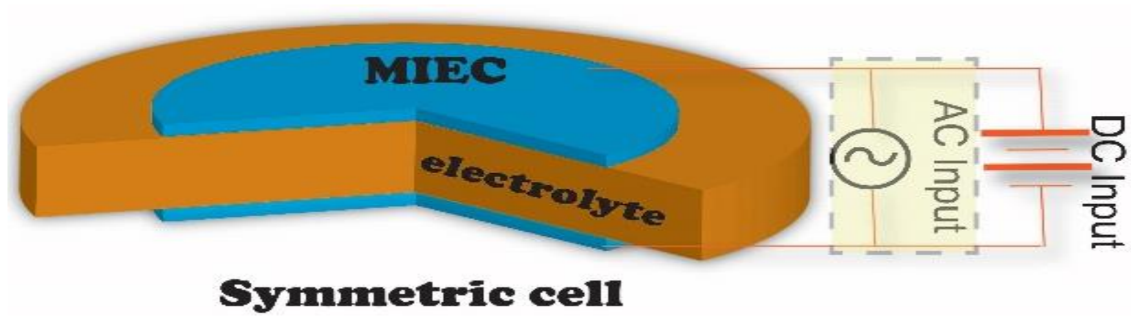
Constant A assumption?

Applicability and Accuracy of both theories?

MIEC electrode vs MIEC electrolyte?

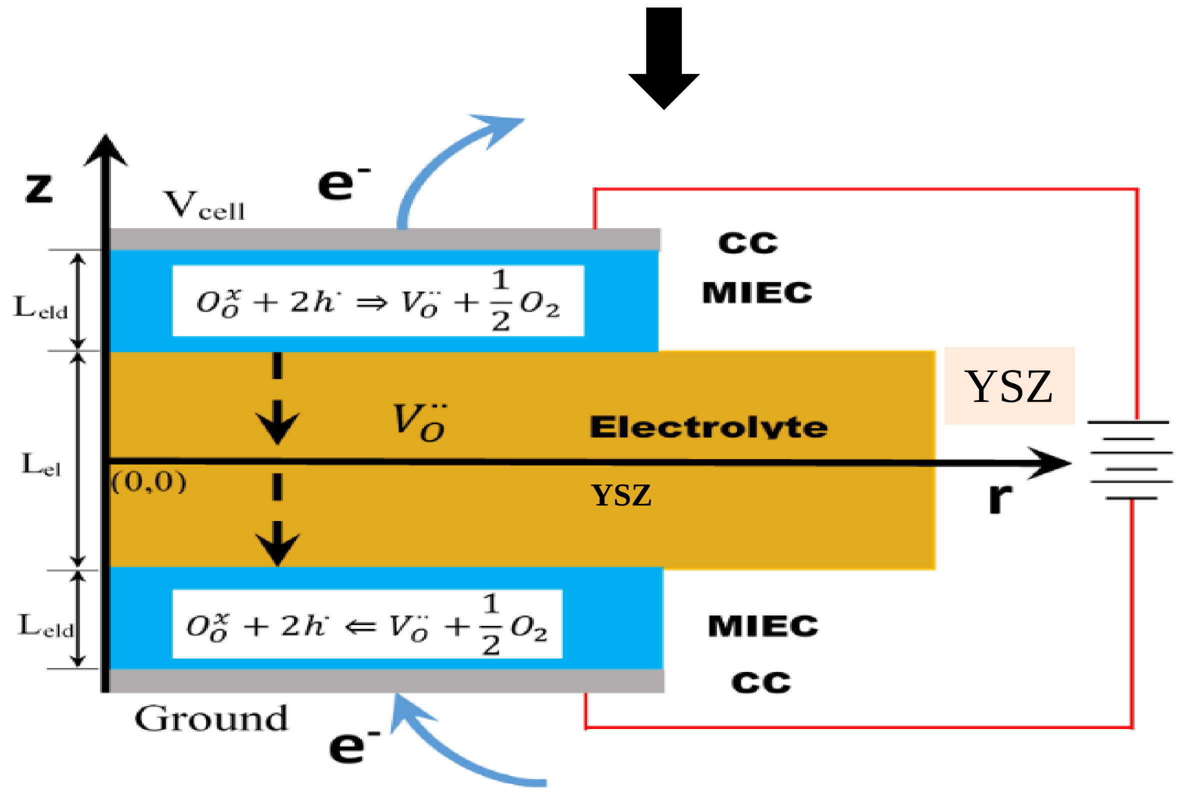
Application in MIEC electrode

(a)



$La_{1-x}Sr_xCoO_{3-\delta}$

(b)



MIEC electrode: Nernst-Planck

3 variables governed by 3 equations

Charge conservations

$$(1-\varepsilon)\frac{\partial \mathrm{c_j}}{\partial \mathrm{t}} = -\nabla\cdot\left(-\mathrm{D_j}\nabla \mathrm{c_j} - \frac{\mathrm{c_j z_j F D_j}}{\mathrm{R}_g \mathrm{T}}\nabla\phi\right) + R_j$$

Charge-Neutrality

$$z_B c_B + \sum_j z_j c_j = z_B c_B + z_v c_v + z_h c_h = 0$$

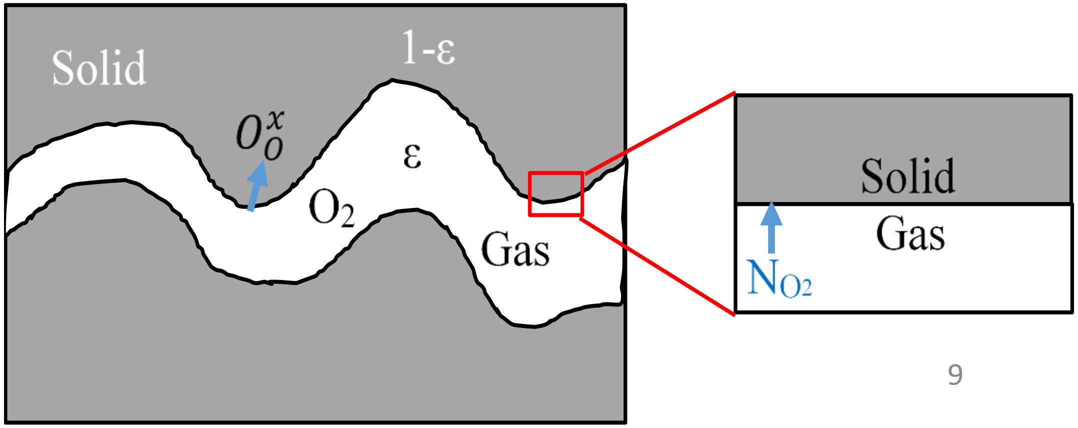
Source terms

$$O_2(g) + 2V_O^{\bullet\bullet} = 2O_O^x + 4h^{\bullet}$$

$$N_{O_2} = -k_{ex}^0 \frac{\mu_{O_2}^{solid} - \mu_{O_2}^{gas}}{\mathrm{R}_g T} = k_{ex}^0 \frac{\mu_{O_2}^{gas} - \mu_{O_2}^{solid}}{\mathrm{R}_g T}$$

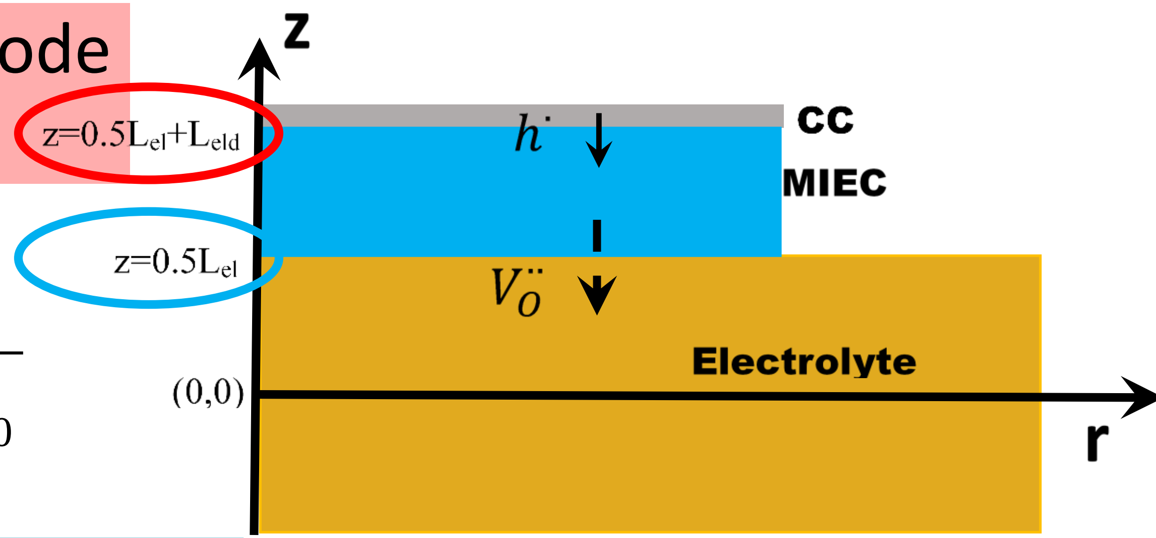
$$R_v = k_v S_a \left(1 + 4\frac{c_{v,0}}{c_{h,0}}\right)\left(c_{v,0} - c_v\right)$$

$$R_h = -2R_v = -2k_v S_a \left(1 + 4\frac{c_{v,0}}{c_{h,0}}\right)\left(c_{v,0} - c_v\right)$$



MIEC electrode: Nernst-Planck

Current collector/electrode interface



$$\phi_{eld} = V_{cell} - \frac{R_g T}{F} \ln \frac{c_{h,eld}}{c_{h,eld,0}}$$

Electrode/electrolyte interface

$$j_{\mathrm{v}} = \frac{C_{dl}\partial \eta}{\partial t} + i_0 \left[\exp\left(\frac{\alpha_1 F}{\mathrm{R}_g T} \eta \right) - \exp\left(-\frac{\alpha_2 F}{\mathrm{R}_g T} \eta \right) \right]$$

$$\eta = \frac{RT}{z_v F} \ln \frac{c_{v,eld}}{c_{v,eld,0}} + \phi_{eld} - \phi_{el}$$

MIEC electrode: Modified Fick's law

1 variables governed by 1 equation

$$(1-\varepsilon)\frac{\partial \mathrm{c_j}}{\partial \mathrm{t}}+\nabla\cdot\left(-A\mathrm{D_j}\nabla c_j\right)=R_j \qquad A=1+\frac{z_v{}^2 c_v}{z_h{}^2 c_h}=1+\frac{4c_v}{c_h}$$

Source terms

$$R_v=k_v S_a\left(1+4\frac{c_{v,0}}{c_{h,0}}\right)\left(c_{v,0}-c_v\right)=Ak_v S_a\left(c_{v,0}-c_v\right)$$

Current collector/electrode interface

$$N_{\mathbf{v}}=0$$

Electrode/electrolyte interface

$$-\frac{2FV_{cell}}{AR_gT}=\frac{x_v^{eld}-x_{v,0}^{eld}}{x_{v,0}^{eld}}$$

How to relate N-P with Fick's

Uniform Fermi Level assumption

$$\nabla \mu_h = \nabla\left(R_g T \ln c_h f_h + z_h F \phi\right) = 0$$

Electrochemical potential of oxygen vacancies

$$\nabla \mu_j = \nabla\left(\mu_j - \frac{z_j}{z_h}\mu_h\right) + \frac{z_j}{z_h}\nabla\mu_h$$

$$= \nabla\left[R_g T \ln c_j f_j + z_j F\phi - \frac{z_j}{z_h}\left(R_g T \ln c_h f_h + z_h F\phi\right)\right] + \frac{z_j}{z_h}\nabla\mu_h$$

$$= \nabla\left[R_g T \ln c_j f_j - \frac{z_j}{z_h} R_g T \ln c_h f_h\right] + \frac{z_j}{z_h}\nabla\mu_h$$

$$= R_g T \nabla \ln c_j + R_g T \nabla \ln f_{j,h} - \frac{z_j}{z_h} R_g T \nabla \ln c_h + \frac{z_j}{z_h}\nabla\mu_h$$

Flux of oxygen vacancies

$$\mathbf{N_j} = -\frac{c_j D_j}{R_g T}\nabla\mu_j$$

$$= -\frac{c_j D_j}{R_g T}\left(R_g T\nabla \ln c_j + R_g T \nabla \ln f_{j,h} - \frac{z_j}{z_h} R_g T \nabla \ln c_h\right)$$

$$= -c_j D_j \left(\nabla \ln c_j + \nabla \ln f_{j,h} - \frac{z_j}{z_h}\nabla \ln c_h\right)$$

$$= -c_j D_j \sum_{i=1,2,3}\left(\frac{\partial \ln c_j}{\partial x}\mathbf{e}_i + \frac{\partial \ln f_{j,h}}{\partial x}\mathbf{e}_i - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial x}\mathbf{e}_i\right)$$

$$= -c_j D_j \sum_{i=1,2,3}\left(\frac{\partial \ln c_j}{\partial \ln c_j}\frac{\partial \ln c_j}{\partial x}\mathbf{e}_i + \frac{\partial \ln f_{j,h}}{\partial \ln c_j}\frac{\partial \ln c_j}{\partial x}\mathbf{e}_i - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial \ln c_j}\frac{\partial \ln c_j}{\partial x}\mathbf{e}_i\right)$$

$$= -c_j D_j \sum_{i=1,2,3}\left(\frac{\partial \ln c_j}{\partial \ln c_j} + \frac{\partial \ln f_{j,h}}{\partial \ln c_j} - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial \ln c_j}\right)\frac{\partial \ln c_j}{\partial x}\mathbf{e}_i$$

$$= -D_j \sum_{i=1,2,3}\left(1 + \frac{\partial \ln f_{j,h}}{\partial \ln c_j} - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial \ln c_j}\right)\frac{\partial c_j}{\partial x}\mathbf{e}_i$$

$$= -D_j \left(1 + \frac{\partial \ln f_{j,h}}{\partial \ln c_j} - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial \ln c_j}\right)\nabla c_j$$

$$= -z_j F D_j A \nabla c_j$$

Thermodynamic factor

$$A = 1 + \frac{\partial \ln f_{j,h}}{\partial \ln c_j} - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial \ln c_j}$$

Thermodynamic factor $D_j = D_j A$

Gas Phase

$$A = \frac{1}{R_g T}\frac{\partial \mu_v}{\partial \ln x_v} = -\frac{1}{R_g T}\frac{\partial \mu_O}{\partial \ln x_v} = -\frac{1}{R_g T}\frac{\partial\left(\mu_O{}^0 + R_g T \ln\sqrt{p_{O_2}}\right)}{\partial \ln x_v} = -\frac{1}{2}\frac{\partial \ln p_{O_2}}{\partial \ln x_v}$$

Solid Phase

$$A = \frac{1}{R_g T}\frac{\partial \mu_j}{\partial \ln c_j} = 1 + \frac{\partial \ln f_{j,h}}{\partial \ln c_j} - \frac{z_j}{z_h}\frac{\partial \ln c_h}{\partial \ln c_j} + \frac{z_j}{z_h}\frac{1}{R_g T}\frac{\partial \mu_h}{\partial \ln c_j}$$

$$W = t_h\left[\frac{\partial \ln a_v}{\partial \ln c_v} - \frac{z_v}{z_h}\frac{\partial \ln a_h}{\partial \ln c_v}\right] = t_h\left[1 + \left(\frac{z_v}{z_h}\right)^2 \frac{c_v}{c_h}\right] = t_h A$$

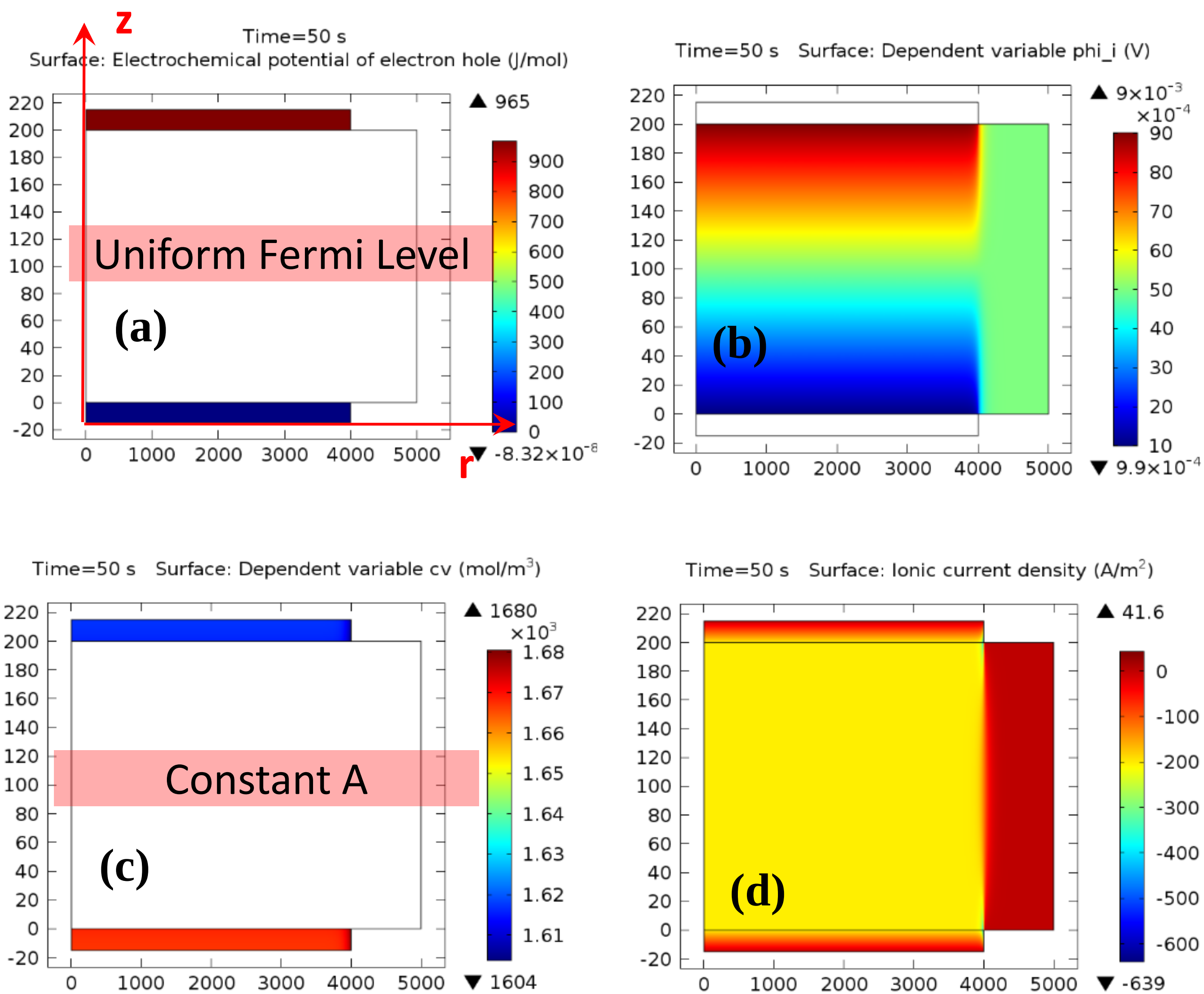
A vs W

Method	Weppner and Huggins 1977 [8]	Adler 1996 [18]
Modified Fick's equation	$\mathbf{N_j} = -\mathrm{D_j} W \nabla c_j$	$\mathbf{N_j} = -\mathrm{D_j} A \nabla c_j$
Definition of W and A	$W = t_h \left[\frac{\partial \ln a_v}{\partial \ln c_v} - \frac{z_v}{z_h} \frac{\partial \ln a_h}{\partial \ln c_v} \right]$	$A = 1 + \frac{\partial \ln f_{j,h}}{\partial \ln c_j} - \frac{z_j}{z_h} \frac{\partial \ln c_h}{\partial \ln c_j}$
Assumption	$\sum_j z_j N_j = 0 \text{ or } \nabla t_v = 0$	Uniform Fermi level $\nabla \mu_h = 0$
Relationship	$W = t_h \left[1 + \left(\frac{z_v}{z_h} \right)^2 \frac{c_v}{c_h} \right] = t_h A$ with f_i=constant, i=v and h.	

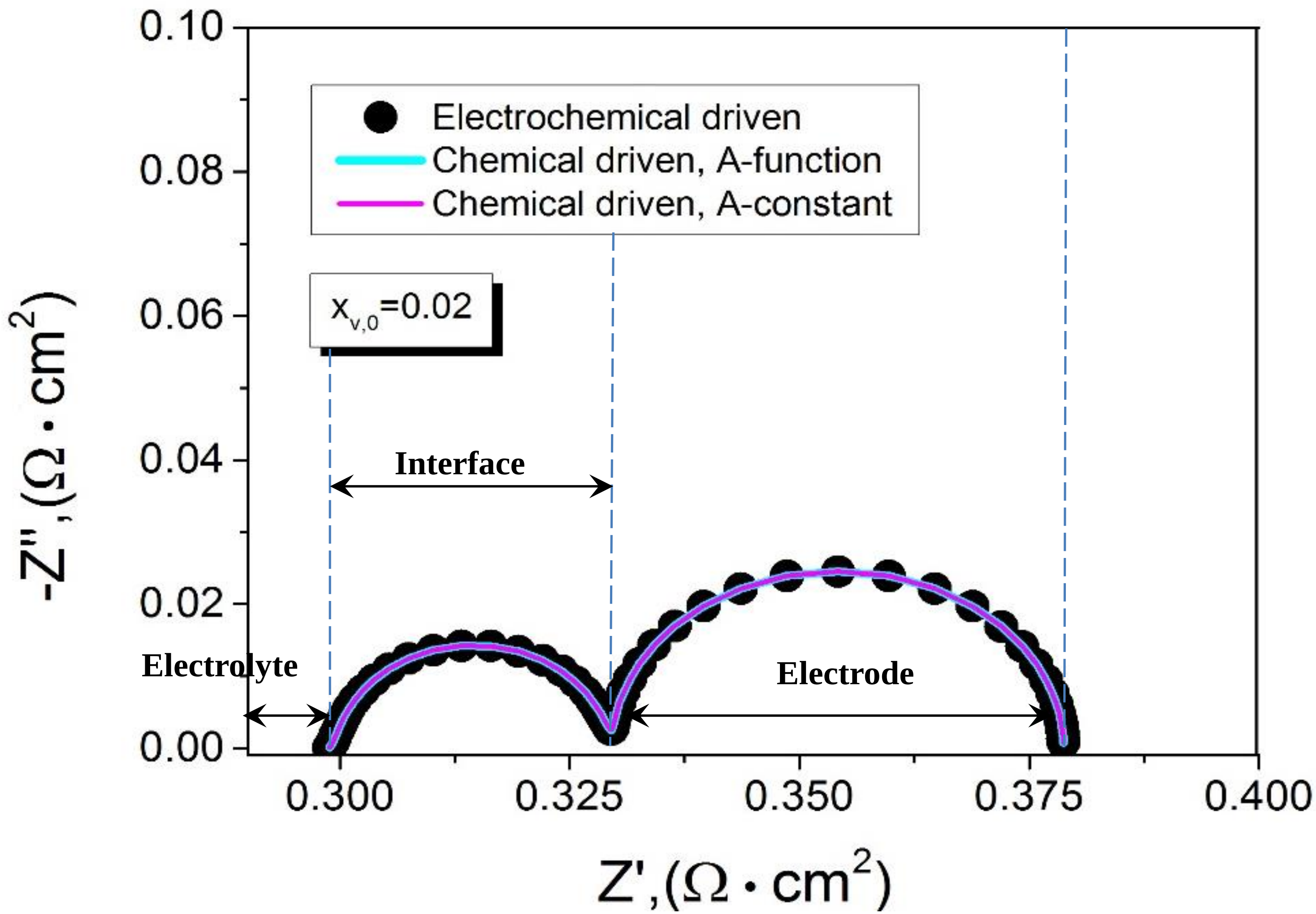
- W derived when $\sum_j z_j N_j = 0$ or t_v=constant;
- For MIEC electrode, W≈A. Uniform Fermi level is equivalent to constant t_v.

Journal of the Electrochemical Society, 1977. **124**(10): p. 1569-1578.
Journal of the Electrochemical Society, 1996. 143(11): p. 3554-3564.

Transient solution: Nernst-Planck

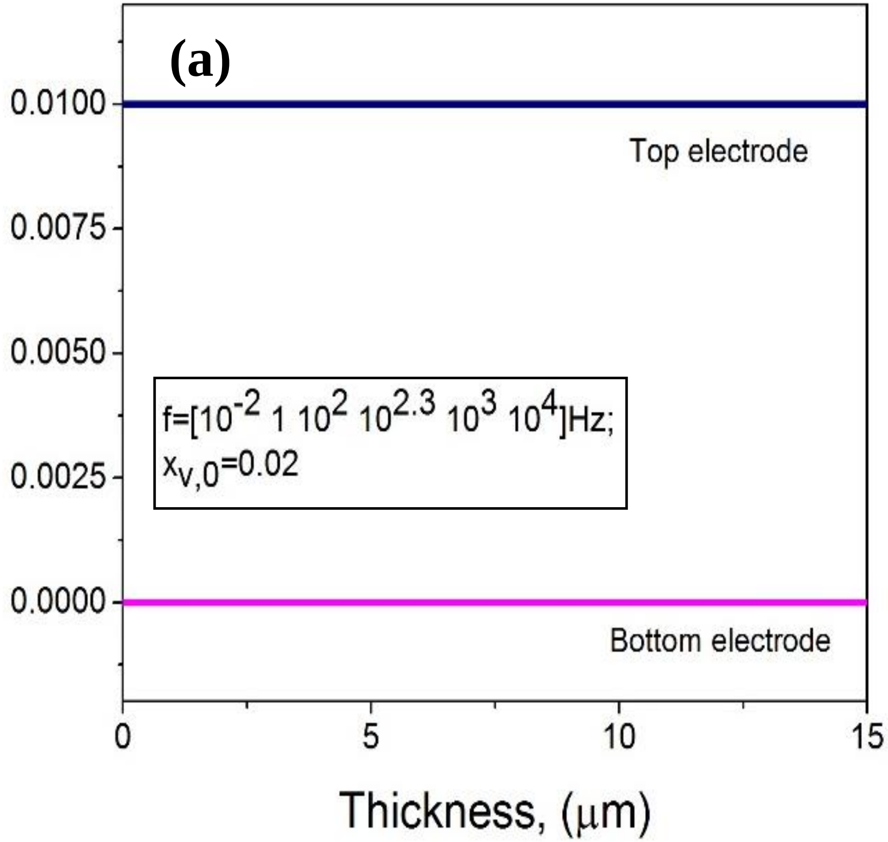


Impedance solutions: N-P vs Fick's

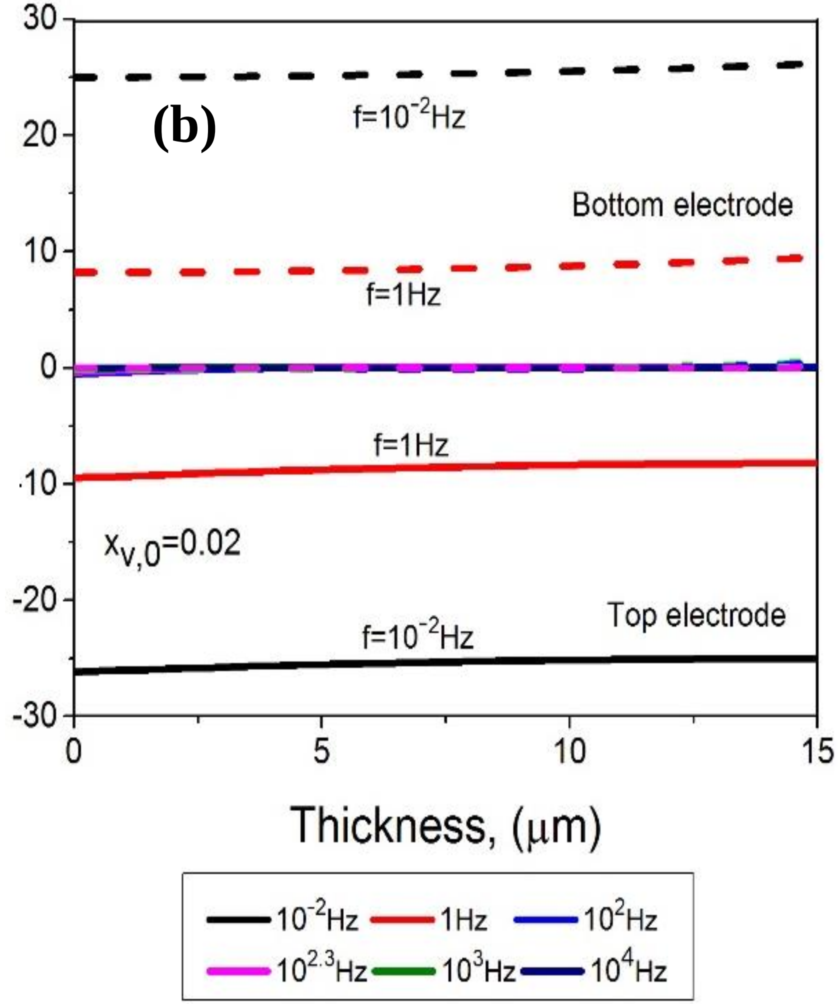


Distribution Profiles: N-P

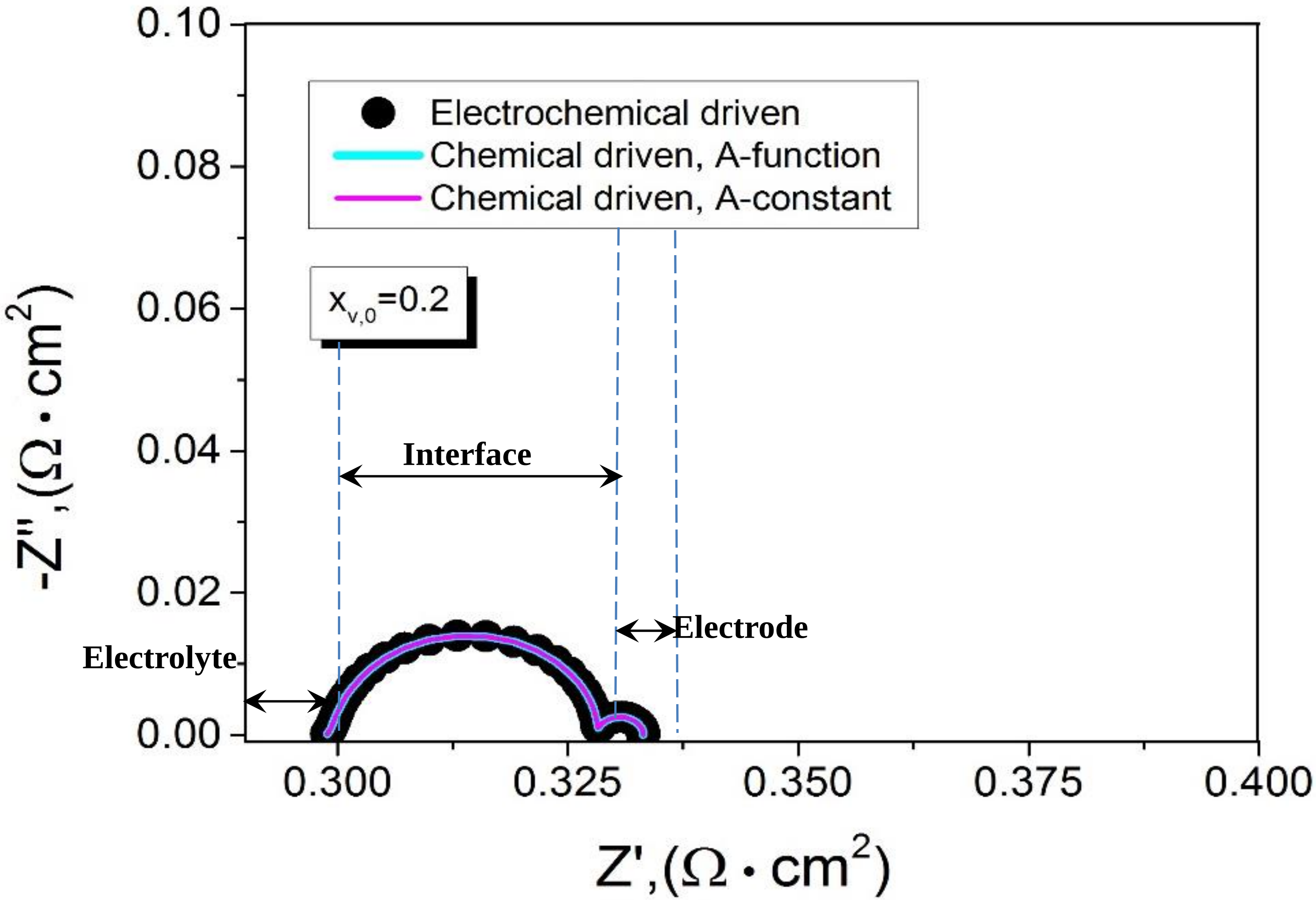
Fermi Level



c_v

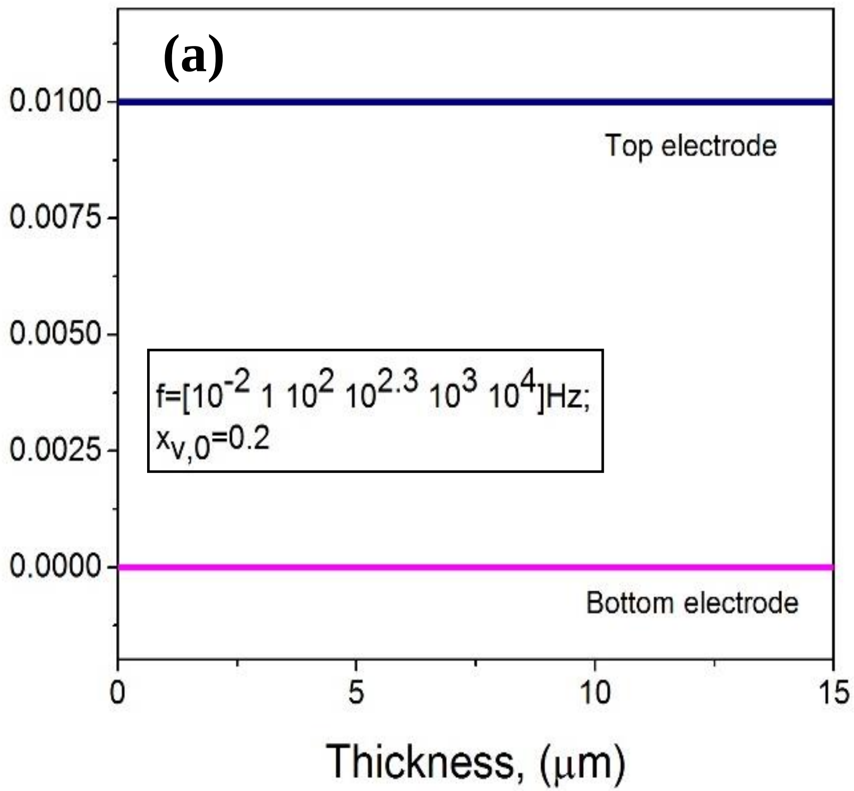


Impedance solutions: N-P vs Fick's

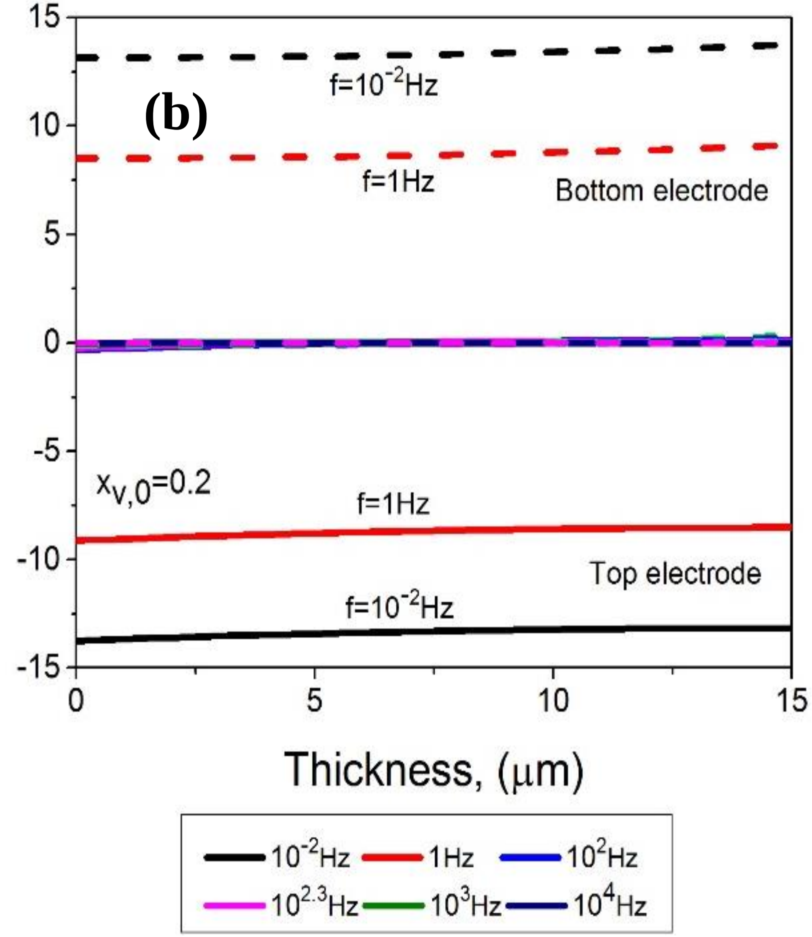


Distribution Profiles: N-P

Fermi Level



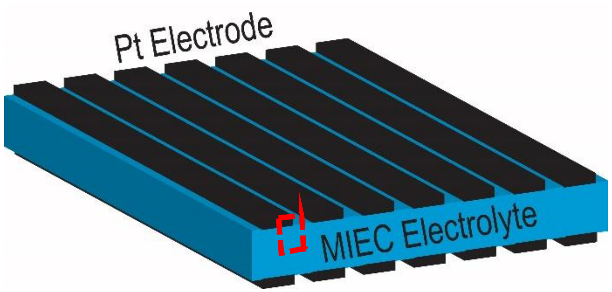
c_v



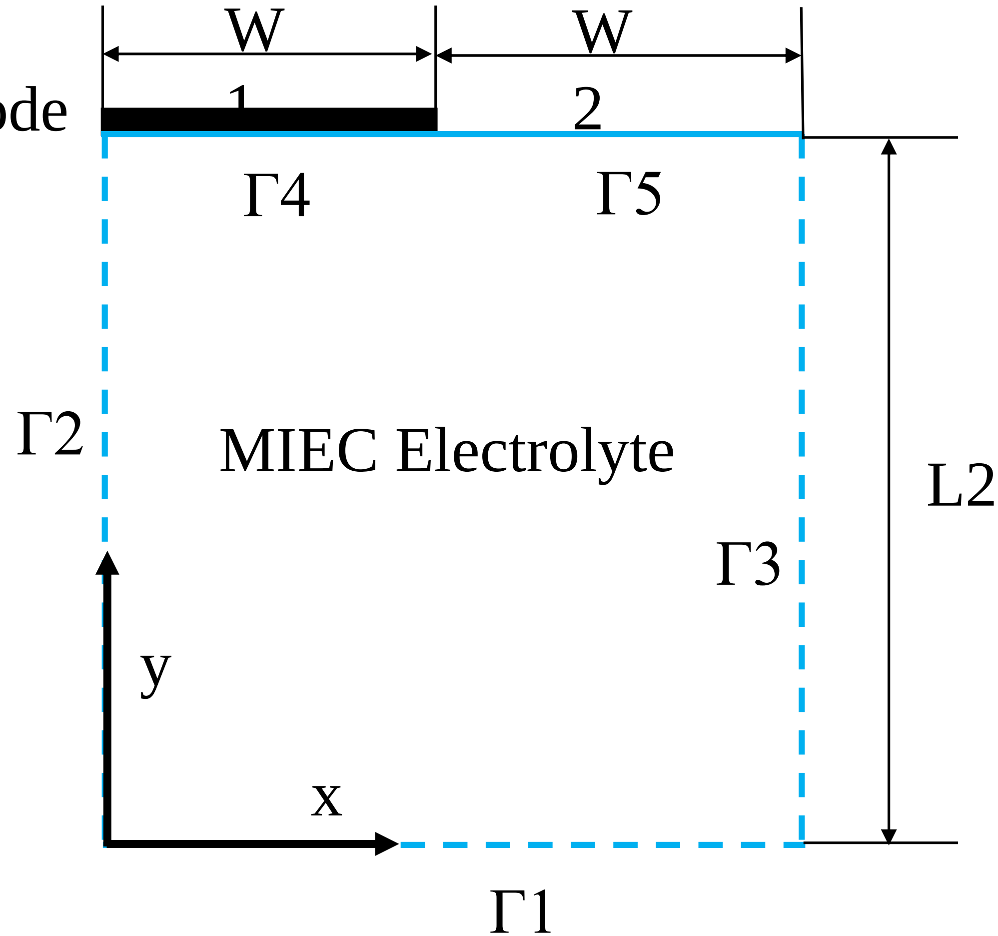
Conclusion: MIEC electrode

- For MIEC electrode with high electronic conductivity, Fermi level is uniform and A is a constant.
- Both N-P and modified Fick's law are applicable.
- For modified Fick's law, A is a function of T and Po_2.

Application in MIEC electrolyte

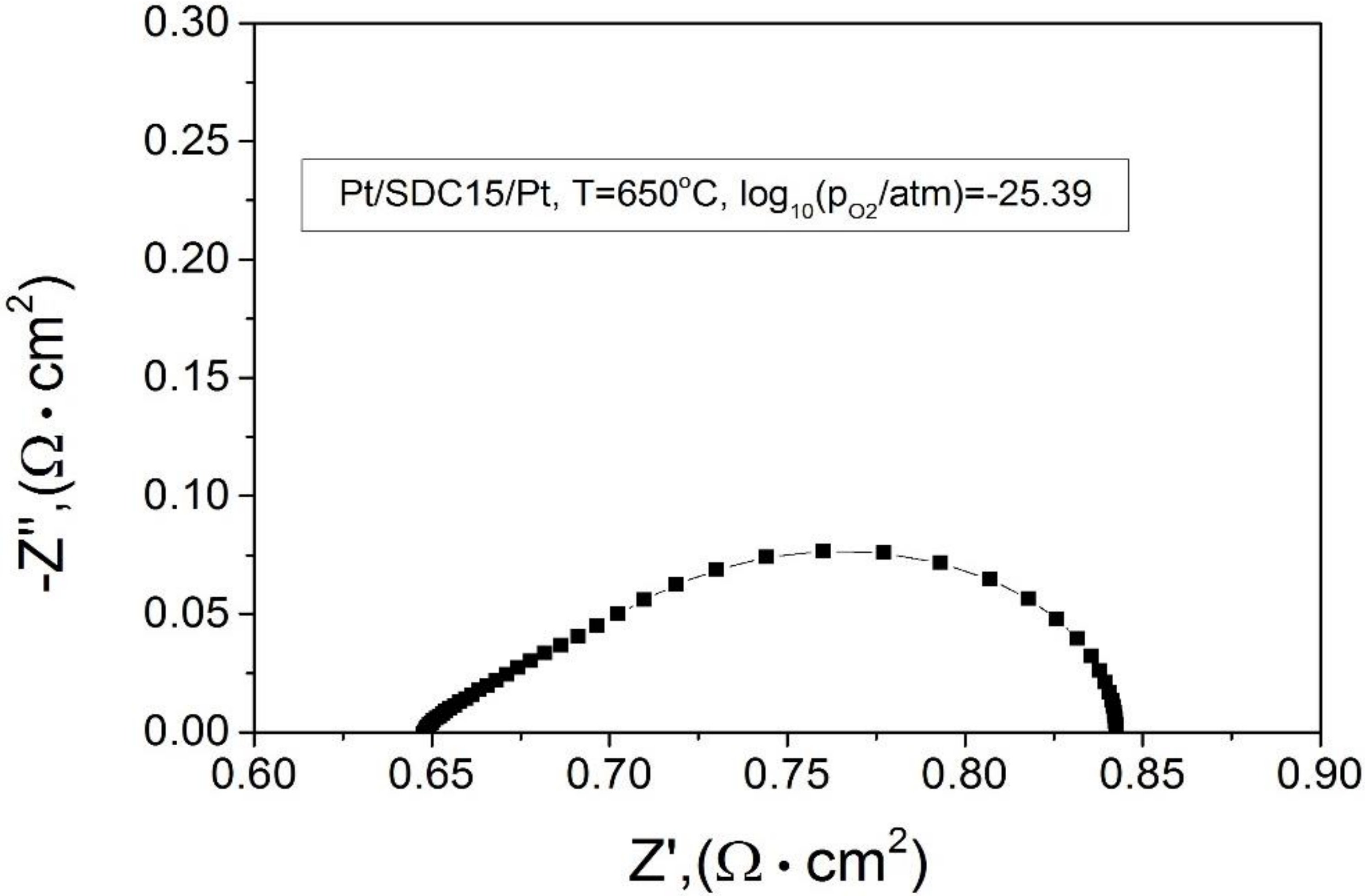


15 mol%-samaria doped ceria (SDC)



Physical Chemistry Chemical Physics, 2009. **11**(47): p. 11243-11257.

Impedance: Nernst Planck

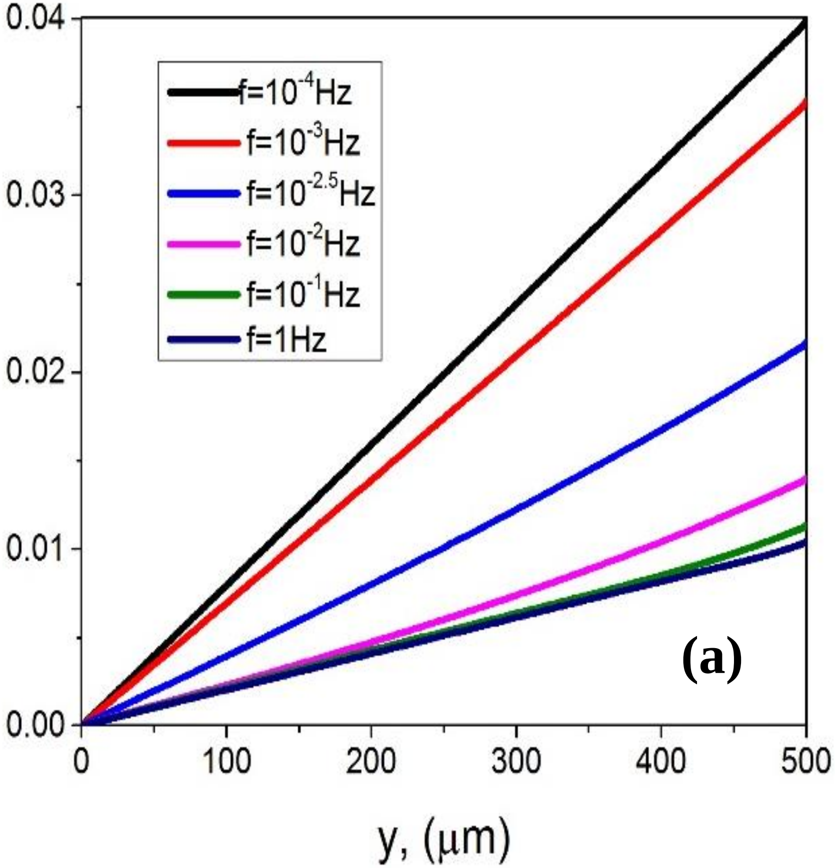


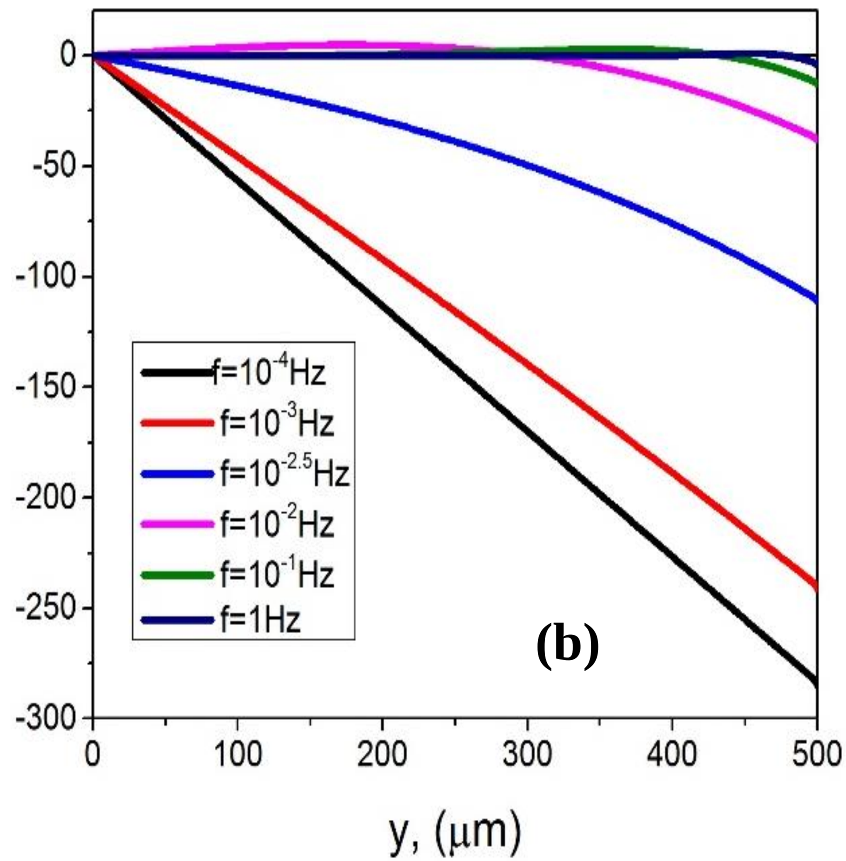
Physical Chemistry Chemical Physics, 2009. **11**(47): p. 11243-11257.

Distribution Profiles: N-P

Fermi Level

c_v





Conclusions: MIEC electrolyte

- For MIEC electrolyte with high ionic conductivity, Fermi level is not uniform and A is not a constant.
- Only N-P is applicable.
- Modified Fick's law could not be used to simplify the model.

Discussions: N-P vs modified Fick's

N-P **VS** **Modified Fick's**

N-P	Modified Fick's
Pros: ✓ 3 variables governed by 3 equations ✓ applicable under all circumstances	**Pros:** ✓ 1 variable governed by 1 equation ✓ easy and simple to implement
Cons: ✓ Complicated and takes more time ✓ Not practical for interpreting experimental data	**Cons:** ✓ only applicable for MIEC electrode with a high electronic conductivity ✓ Must be very careful to set boundary conditions

Future work-Wagner's Work

$$c_i \nabla \mu_i = \sum_j K_{ij}(\mathbf{v}_j - \mathbf{v}_i) = RT \sum_j \frac{c_i c_j}{c_T \mathscr{D}_{ij}} (\mathbf{v}_j - \mathbf{v}_i),$$

Link Liquid solution theory to solid solution theory

$$\nabla \mu_j = R_g T \nabla \ln c_j + z_j F \nabla \phi$$

J. Electrochem. Soc., 145(1),1998,143

Thanks for your attention!