Poisson-Nernst-Planck Simulator (PoNPs) Manual

[Abstract]

The PoNPs code is a Numerical simulator for the one-dimensional Poisson-Nernst-Planck (1D-PNP) systems. The 1D-PNP equations are numerically solved, to acquire the time dependences of charge-carrier concentration profiles and electric potential (or electric field) profile. A steady state (constant current), a transition process from a steady state to another, and an impedance spectrum can be analyzed. The diffusion coefficients of all charge carriers should be specified for each of multiple layers. In addition, the rate constants and standard Gibbs energy changes of inter-layer and intra-layer reactions should also be specified. Both ends of a given system contact reservoirs of charge carriers, where the concentration of each charge carrier is constant at a given value.

Since the PoNPs code was written for all-solid-state systems, charge carriers are hereafter called *defects* in crystals. This code is applicable to any systems including charge-neutral defects and/or liquid and gas phases in principle, although the convection cannot be treated.

The PoNPs code was written by Kazuaki Toyoura. Dr. Katsuhiro Ueno has great contribution to the code development with many bug reports and fruitful discussions based on electrochemistry and defect chemistry. The following paper is referred for writing this code, and several advanced features are newly added in PoNPs.

T. R. Brumleve and R. P. Buck, Numerical solution of the Nernst-Planck and Poisson equation system with applications to membrane electrochemistry and solid state physics, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **90**, 1-31 (1978).
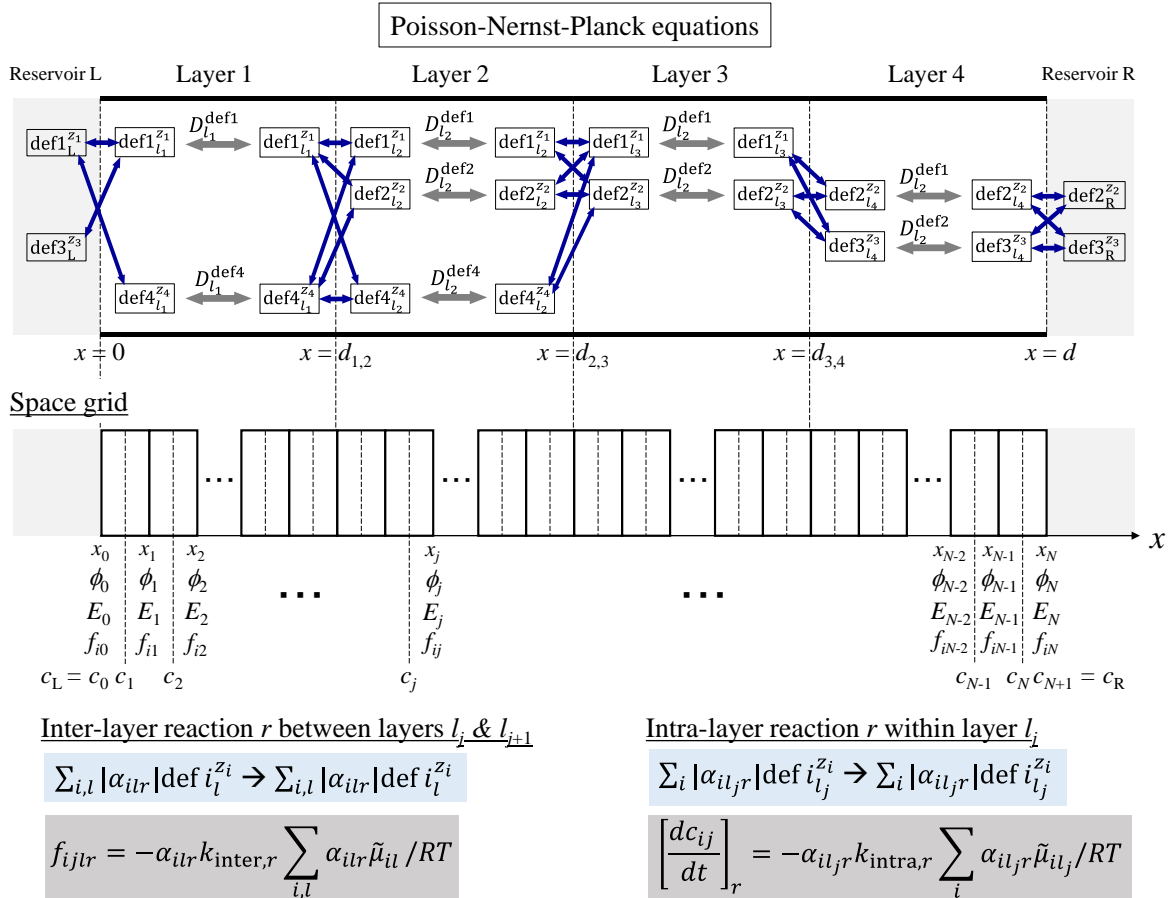

Inter-layer reaction r between layers l_j & l_{j+1}

$$\sum_{i,l} |\alpha_{ilr}| \operatorname{def} i_l^{z_i} \rightarrow \sum_{i,l} |\alpha_{ilr}| \operatorname{def} i_l^{z_i}$$

$$f_{ijlr} = -\alpha_{ilr} k_{\text{inter},r} \sum_{i,l} \alpha_{ilr} \tilde{\mu}_{il} / RT$$

Intra-layer reaction r within layer l_j

$$\sum_i |\alpha_{il_jr}| \operatorname{def} i_{l_j}^{z_i} \rightarrow \sum_i |\alpha_{il_jr}| \operatorname{def} i_{l_j}^{z_i}$$

$$\left[\frac{dc_{ij}}{dt}\right]_r = -\alpha_{il_jr} k_{\text{intra},r} \sum_i \alpha_{il_jr} \tilde{\mu}_{il_j} / RT$$

Fig. 1 Schematic drawing of the PoNPs code

[Programming language]

Python 3.x (installed through anaconda, https://www.anaconda.com/products/individual)

Imported modules in this code: numpy, scipy, matplotlib, argparse, copy, datetime, os, sys

[Input files]

All input files have to be prepared in the csv format. The last three are optional.

comp.csv: Computational conditions

defect.csv: Information on all defect species

layer.csv: Information on all layers in a system

reaction.csv: Information on all interlayer and intralayer reactions

conc.csv: Initial profiles of all defect species

efield.csv: Initial profile of electric field

spaceGrid_*layerID*.csv (optional): Space grid intervals in a layer (File name is specified in layer.csv. Separated files are required for individual layers.)

timeGrid.csv (optional): Information on the time grid (File name is specified in comp.csv.)

freqGrid.csv (optional): Information on the frequency for impedance spectroscopy (File name is specified in comp.csv.)

[Output files]

conc_fin.csv: Final profiles of all defect species (Please use this file as conc.csv for continuation.)

efield_fin.csv: Final profiles of electric field (Please use this file as conc.csv for continuation.)

voltage_profile.csv: Time dependence of voltage between both ends

phi_profile.csv: Time dependence of electric potential profile

conc*defectID*_profile.csv: Time dependence of concentration profile of each defect species

partialI*defectID*_profile.csv: The profile of partial current for each defect species

impedance.csv: Information on impedance spectrum (Output only for impedance simulations)

profile_*timeStep*.pdf: Figures for the profiles of defect concentrations and electric potential at selected time steps. The *x* axis is shown in the length scale, cm.

profile_xid_*timeStep*.pdf: Same information on profile_*timeStep*.pdf. The *x* axis is shown by space grid id.

impedance.pdf: Nyquist plot (Output only for impedance simulations)

Bode.pdf: Bode diagram (Output only for impedance simulations)

[Usage]

Type the following command at the directory with the required six files (+ optional files).

Default names (comp.csv, defect.csv, layer.csv, reaction.csv, conc.csv, efield.csv) can be skipped.

python [PONPS_DIR]/ponps.py --comp comp.csv --defect defect.csv --layer layer.csv --reaction reaction.csv --conc conc.csv --efield efield.csv

[Details for input and output files]

Input files

[comp.csv]

"#" denotes comment lines. Put each item separated by comma.

Line 1: Basic computational conditions

calcType: Choose calculation type out of the following two types.

> time_evolution: Simulation for time evolution of a given system with initial conditions.

> impedance: Simulation for impedance spectroscopy. The profiles of defect concentrations and electric field in the steady state should be prepared by time_evolution simulations as a pre-process. The two files of conc_fin.csv and efield_fin.csv in the steady state are used as conc.csv and efield.csv in the the impedance simulation. A small perturbation current is additionally required in the impedance simulation.

Temperature [K]: Temperature of the system.

I [A/cm^2]: Current density.

n_print [integer]: n_print lines are output in the profile files. If $n\_print = 0$, information at all time steps are output. n_print time steps are sampled at equal intervals for output at $n\_print > 0$, while n_print time steps are sampled according to the change in total voltage between both ends at $n\_print < 0$.

n_figs [integer]: Profiles of defect concentrations and electric field are output n_figs times during the simulation.

Line 2: Conditions of the Newton-Raphson (NR) method

iter_max [integer]: Maximum iterations.

prec_c: Convergence criterion for defect concentrations. The NR iteration is terminated when the change rates of all defect concentrations at all positions become less than prec_c.

prec_E: Convergence criterion for electric field. The NR iteration is terminated when the change rates at all positions become less than prec_E.

n_switch [integer]: NR iteration number for switching the convergence conditions. When NR iteration number < n_switch, the convergence condition is based on the defect concentrations and electric fields. When NR iteration >= n_switch, the convergence condition is based on the total voltage between both ends. If the switching is not necessary, n_switch should be larger than $iter\_max$.

prec_Volt [V]: Convergence criterion for the total voltage between both ends. The NR iteration is terminated when the change (not change rate) in total voltage becomes less than $prec\_Volt$.

Line 3: Setting parameters for time grid

mkTimeGrid: The way to make time grid.

> auto: The time grid is automatically calculated by geometric sequence using the subsequent parameters. The Minimum & maximum time intervals should be specified.

> File name [string]: File name containing time-grid information, e.g., timeGrid.csv. This file should be written in the csv format.

dt_max [s]: The maximum time interval, which is used only at *mkTimeGrid* = auto.

        If *dt_max* = auto, the maximum time interval is set to Debye time, τ_d.

        Even if the time grid file is specified by *mkTimeGrid*, this item cannot be skipped.

dt_min [s]: The minimum time interval, which is used only at *mkTimeGrid* = auto.

        If *dt_min* = auto, the minimum time interval is set to $\tau_\infty/100$, where τ_∞ denotes the smallest time constant.

        τ_∞ is given by $\tau_\infty = (\varepsilon RT/F^2)/\Sigma z_i^2 D_i c_{i,\text{ave}}$, where R is the gas constant, T is the absolute temperature, and

        F is the Faraday constant. z_i, D_i, and $c_{i,\text{ave}}$ are the valence, diffusion coefficient, and average concentration

        of defect i, respectively. Even if timeGrid.csv is specified by *mkTimeGrid*, this item cannot be skipped.

n_timeSteps [integer]: Total number of time steps. Even if the time grid file is specified by *mkTimeGrid*, this item cannot be skipped.

n_dt_max [integer]: The time intervals at the last *n_dt_max* steps are set to be dt_max. (n_dt_max ≤ n_timeSteps).

Line 4: Setting for impedance (Even if *calcType* = time_evolution, this line cannot be skipped.)

Delta I [A/cm^2] : Small current density as a perturbation for impedance simulations.

mkFreqGrid: The way to make frequency grid.

        auto: Frequency grid is automatically generated by geometric sequence using the subsequent parameters.

        File name [string]: The file name with frequency information, e.g., freqGrid.csv. This file should be written in the csv format.

freq_max [Hz]: The maximum frequency, which is used only at *mkFreqGrid* = auto.

        Even if the frequency file is specified by *mkFreqGrid*, this item cannot be skipped.

freq_min [Hz]: The minimum frequency, which is used only at *mkFreqGrid* = auto.

        Even if the frequency file is specified by *mkFreqGrid*, this item cannot be skipped.

n_freqSteps [integer]: Total number of frequencies. Even if freqGrid.csv is specified by mkFreqGrid, this item cannot be skipped.

(Example)
```
#Basic setting
#calcType,temperature[K],I[A/cm2],n_print,n_figs
time_evolution,773.15,0.1,100,10
#Setting for Newton-Raphson method
#iter_max,prec_c,prec_E,n_switch,prec_Volt[V]
100,1.0e-4,1.0e-4,10,1.0e-10
#Time grid setting
#mkTimeGrid,dt_max[s],dt_min[s],n_timeSteps,n_dt_max
auto,auto,auto,1000,10
#Setting for impedance spectroscopy
#delta_I[A/cm2],mkFreqGrid,freq_max[Hz],freq_min[Hz],n_freqSteps
0.001,auto,1.0e+9,1.0e-6,300
```

defect.csv

"#" denotes comment lines. Put each item separated by comma. New line for different defect species.

Immobile defect species are *not necessary*, even if it is necessary for charge compensation in the system.

DefectName: Name of defect species.

z: valence of the defect species.

c_L [mol/cm^3]: Defect concentration in reservoir at the left end.

c_R [mol/cm^3]: Defect concentration in reservoir at the right end.

c_{LB} [mol/cm^3]: Lower bound for Defect concentration.

When some defect concentrations become lower than c_{LB} during the NR process, the low concentrations are replaced by c_{LB}. Any defect concentration should be positive, because the reaction rate is proportional to log c. When warning on this replacement is output in the log file, simulation results should be checked carefully. The simulation conditions have to be tuned in such cases.

c_{UB} [mol/cm^3]: Upper bound for Defect concentration.

When some defect concentrations become higher than c_{UB} during the NR process, the high concentrations are replaced by c_{UB}. Note that defect concentrations can become more than the total number of defect sites. When warning on this replacement is output in the log file, simulation results should be checked carefully. The simulation conditions have to be tuned in such cases.

D [cm^2/s] : Diffusion coefficients in individual layers. Put each value separated by comma.

(Example)

#defectName,z,cL[mol/cm3],cR[mol/cm3],cLB[mol/cm3],cUB[mol/cm3],D1[cm2/s],D2[cm2/s],...

H,1,0.003391557,0.003391557,0.0,0.066225165,4.05E-07

VO,2,0.000511727,0.000511727,0.0,0.066225165,3.62E-09

h,1,3.19E-11,3.19E-11,0.0,0.066225165,1.30E-06

#Y,-1,0.004415011,0.004415011,0.0,0.066225165,0.0   # Immobile

layer.csv

"#" denotes comment lines. Put each item separated by comma. New line for different layers.

layerName: Layer name.

epsilon_r: Relative permittivity.

length [cm]: The length of the layer.

mkSpaceGrid: The way to make frequency grid.

auto: The space grid is automatically generated by geometric sequence using the subsequent parameters. Only for the regions near both ends of the layer, an equally spaced fine grid is used. Specifically, the regions close to both ends up to several times of the Debye length inside (*n_ldebye* times of *ldebye* inside) are divided into several elements per the Debye length (*n_elem_ldebye* elements per *ldebye*).

File name [string]: The file name with information on the space grid in the layer, e.g., spaceGrid.csv. This file should be written in the csv format, and all grid intervals are given in cm.

n_elements [odd integer]: The number of space elements in the layer, which is used only at *mkSpaceGrid* = auto. Even if the space grid file is specified by *mkSpaceGrid*, this item cannot be skipped.

ldebye [cm]: Debye length, which is used only at *mkSpaceGrid* = auto. If *ldebye* = auto, the Debye length is automatically estimated from the information in the input files.

n_elem_ldebye [integer]: Number of space elements in the Debye length, which is used only at *mkSpaceGrid* = auto.

n_ldebye [integer]: The region with an equally spaced fine grid is specified as *n_ldebye*-times Debye length, which is used only at *mkSpaceGrid* = auto.

slowestDefect [positive integer]: ID of the slowest defect species in the layer, corresponding to the line number in defect.csv. This is used only for *dt_max* = auto in comp.csv.

(Example)

#layerName,epsilon_r,length[cm],mkSpaceGrid,n_elements,ldebye[cm],n_elem_ldebye,n_ldebye,slowDefectID

LYTE1,62,0.2,auto,201,auto,5,4,2

LYTE2,62,0.1,auto,101,auto,5,4,2

reaction.csv

This file contains information on all intra-layer and inter-layer reactions in a given system.

Intra-layer reaction r is expressed by set $\boldsymbol{\alpha}_r$ of stoichiometric coefficients of all defects $\{\alpha_{ir}\}$ ($i = 1, 2, \ldots, n_{\text{def}}$), where n_{def} is the number of defect species. In the present definition, reactants have a *negative* stoichiometric coefficient, while products have a *positive* coefficient. The reaction rate is assumed to be proportional to the Gibbs energy change of the reaction r, ΔG_r, under the linear response approximation, expressed as follows:

$$[\partial c_i/\partial t]_r = -\alpha_{ir}k_{\text{intra},r}\Delta G_r/RT = -\alpha_{ir}k_{\text{intra},r}\,\Sigma_i\alpha_{ir}\tilde{\mu}_i(x,t)/RT$$
$$= -\alpha_{ir}k_{\text{intra},r}\,(\,\Delta G^0_r + \Sigma_i\alpha_{ir}(\,RT\ln(c_i(x,t)/[\text{mol/cm}^3]) + z_iF\phi\,)\,)\,/\,RT,$$

(R: J/mol·K, T: K, ΔG: J/mol, c_i: mol/cm^3, $k_{\text{intra},r}$: mol/cm^3·s, F: C/mol, ϕ: V)

where $k_{\text{intra},r}$ is the reaction rate, $\tilde{\mu}_i$ and μ_i are the electrochemical potential and chemical potential of defect i, respectively. ΔG^0_r is the standard Gibbs energy change of reaction r, which is specified in **kJ/mol** in reaction.csv. For an intra-layer reaction, the electrochemical potential is equivalent to the chemical potential, because the reaction proceeds within single space elements at the same electric potential ϕ.

For an inter-layer reaction, the reactants and products can exist in the left and right layers to the interface. Therefore, the stoichiometric coefficients should be defined for both left and right layers, which are given as $\boldsymbol{\alpha}_{lr} = \{\alpha_{ilr}\}$ ($i = 1, 2, \ldots, n$, $l = l_j$ and l_{j+1}). As a result, the flux of defect i on the layer l side by reaction r, f_{ijlr}, is given by a similar equation to the above one,

$$f_{ijlr}(x,t) = -\alpha_{ilr}k_{\text{inter},r}\,(\,\Delta G^0_r + \Sigma_{i,\,j'=j,j+1}\alpha_{ilj'r}(\,RT\ln(c_{ij'}/[\text{mol/cm}^3]) + z_iF\phi_{j'}\,)\,)\,/\,RT.$$

Note that the unit of $k_{\text{inter},r}$, **mol/cm^2·s**, is different from that of $k_{\text{intra},r}$, **mol/cm^3·s**.

[File format]

Layers in a system are numbered from left to right including the two reservoirs. The left reservoir L is 0, the first layer is 1, and so on. "#" denotes comment lines. Put each item separated by comma. New line for different reactions.

layer_id_L: ID of left layer for an interlayer reaction. Or layer ID for an intra-layer reaction.

layer_id_R: ID of right layer for an interlayer reaction. Or layer ID for an intra-layer reaction, i.e., = layer_id_L.

stoichCoeff_L $\{\alpha_{iL}\}$: The set of stoichiometric coefficients of all defects in the left layer for an inter-layer reaction.

The set of stoichiometric coefficients in the layer for an intra-layer reaction.

stoichCoeff_R $\{\alpha_{iR}\}$: The set of stoichiometric coefficients of all defects in the right layer for an inter-layer reaction.

~~The set of stoichiometric coefficients in the layer for an intra-layer reaction, i.e., = $\{\alpha_{iL}\}$.~~

For an intra-layer reaction, $\{\alpha_{iR}\}$ is neglected. Any values are acceptable, but cannot be skipped.

k [mol/cm^{3}s or mol/cm^{2}s]: The reaction rate constant.

ΔG^0 [kJ/mol]: The standard Gibbs energy change of the reaction. Note that the unit is **_kJ/mol_**.

(Example)

#layer_id,layer_id,$\alpha_1,\alpha_2,\alpha_3,\alpha_4,\alpha_5,\alpha_1,\alpha_2,\alpha_3,\alpha_4,\alpha_5,k,\Delta G^0$ (Intralayer)

1,1,-1,0,0,2,-3,-1,0,0,2,-3, 1.0E-06,-153.124

#layer_id_L,layer_id_R,$\alpha_{1L},\alpha_{2L},\alpha_{3L},\alpha_{4L},\alpha_{5L},\alpha_{1R},\alpha_{2R},\alpha_{3R},\alpha_{4R},\alpha_{5R},k,\Delta G^0$ (Interlayer)

0,1,-1,0,0,2,0,0,0,0,0,-3,1.0E-09,10.927

conc.csv

"#" denotes comment lines. Put the defect concentration profile [mol/cm^3] separated by comma. New line for different defect species. The order of defect species should be consistent to that in defect.csv. The defect concentration is here defined as the average in each space element. Therefore, the number of defect concentrations in every line have to be equal to the total number of space elements of all layers, not including the reservoir concentrations, c_L and c_R. If conc.csv is insufficient, the initial concentration profile is automatically generated by linearly interpolating logarithmic concentrations between c_L and c_R.

(Example)

Concentration profile of each defect species [mol/cm^3]

1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6,1.0e-6

1.4e-5,1.3e-5,1.2e-5,1.1e-5,1.0e-5,9.0e-6,8.0e-6,7.0e-6,6.0e-6,5.0e-6,4.0e-6,3.0e-6,2.0e-6,1.0e-6

efield.csv

"#" denotes comment lines. Put the electric field profile [V/cm] separated by comma. The electric field is here defined on every boundary between adjacent space elements including the two reservoirs at both ends. Therefore, the number of electric fields have to be greater than the total number of space elements of all layers by one. If efield.csv is insufficient, the initial electric field is set to zero at all positions.

（Example）

Electric field in each element

0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0

spaceGrid_*layerID*.csv (optional)

"#" denotes comment lines. Put the space grid data [cm] separated by comma, which corresponds to the width of every space element. The number of data have to be equal to the number of space elements in the layer.

(Example)

dx [cm] in each element

1.0e-8,1.0e-8,1.0e-7,1.0e-6,1.0e-5,1.0e-4,1.0e-3,1.0e-4,1.0e-5,1.0e-6,1.0e-7,1.0e-8,1.0e-8

timeGrid.csv (optional)

"#" denotes comment lines. Put the time grid data [s] at every time step separated by comma. The number of items have to be equal to the number of time step specified in comp.csv.

(Example)

dt [s] in evergy time grid

1.0e-10,1.0e-9,1.0e-8,1.0e-7,1.0e-6,1.0e-5,1.0e-4,1.0e-3,1.0e-2,1.0e-1,1.0,1.0e+1,1.0e+2

freqGrid.csv (optional)

"#" denotes comment lines. Put the frequency data [/s] for impedance spectroscopy separated by comma. The number of items have to be equal to the total number of frequencies specified in comp.csv.

(Example)

Frequencies [/s] for impedance spectroscopy

1.0e-10,1.0e-9,1.0e-8,1.0e-7,1.0e-6,1.0e-5,1.0e-4,1.0e-3,1.0e-2,1.0e-1,1.0,1.0e+1,1.0e+2

【**Output files**】

conc_fin.csv: Defect concentration profiles in the final state

The file format is the same as that in conc.csv. The time-evolution simulation can continue by using this file as conc.csv. The input file conc.csv in impedance simulations have to be the conc_fin.csv corresponding to the steady state at a constant current I without current perturbation δI.

efield_fin.csv: Electric field profile in the final state

The file format is the same as that in efield.csv. The time-evolution simulation can continue by using this file as efield.csv. The input file efield.csv in impedance simulations have to be the efield_fin.csv corresponding to the steady state at a constant current I without current perturbation δI.

voltage_profile.csv: Time dependence of the total voltage

Time dependence of the total voltage corresponding to the electric potential at the right end vs. the left end.

Line 1: Comment

After line 2: time [s], total voltage [V] separated by comma

phi_profile.csv: Time dependence of electric potential profile

Time dependence of the electric potential profile (vs. that at the left end).

Line 1: Comment

Line 2: nan, the distances from the left end [cm] separated by comma

After line 3: time [s], electric potential [V] at each position separated by comma

conc[*defectID*]_profile.csv: Time dependence of each defect concentration profile

Time dependence of each defect concentration profile. New files for different defect species. Defect ID corresponds to the line number in defect.csv.

Line 1: Comment

Line 2: nan, the distances from the left end [cm] separated by comma

After line 3: time [s], concentration [mol/cm^3] at each position separated by comma

partialI[*defectID*]_profile.csv: Time dependence of partial current density of each defect species

Time dependence of partial current density profile of each defect species. New files for different defect species. Defect ID corresponds to the line number in defect.csv. The partial current densities across a hetero-interface can be different between the left and right sides of the interface. For all hetero-interfaces, both current densities on the left and right sides are output in the file.

Line 1: Comment

Line 2: nan, the distances from the left end [cm] separated by comma

After line 3: time [s], partial current [A/cm^2] at each position separated by comma

impedance.csv: Impedance spectroscopy data

Line 1: Comment

After line 2: Frequency [s], real part of impedance [Ω], and imaginary part of impedance [Ω] separated by comma

profile_[*timeStep*].pdf, profile_xid_[*timeStep*].pdf: Profiles of defect concentrations and electric potentials

Figures of calculated profiles of defect concentrations and electric potentials, which are output *n_figs*-times during the simulation. *n_figs* is specified in comp.csv. The *x* axis corresponds to the distance from the left end [cm] in profile_[*timeStep*].pdf and to the space element id in profile_xid_[*timeStep*].pdf.

impedance.pdf & Bode.pdf: Nyquist plot & Bode diagram

Figures of Nyquist plot and Bode diagram output for impedance simulations.

[Theoretical background]

Governing equations

The PoNPs code is a numerical simulator for the one-dimensional Poisson-Nernst-Planck (1D-PNP) systems. This program numerically solves the 1D-PNP equations, to acquire the time dependences of defect concentrations and electric potentials. The governing equations are the Nernst-Planck equation, the continuity equation, and Poisson's equation as follows:

$$f_i(x,t) = -D_i[\partial c_i(x,t)/\partial x - z_i c_i(x,t)(F/RT)E(x,t)], \tag{1}$$

$$\partial c_i(x,t)/\partial t = -\partial f_i(x,t)/\partial x + \Sigma_r[\partial c_i(x,t)/\partial t]_r, \tag{2}$$

$$\partial E(x,t)/\partial x = (4\pi/\varepsilon)\rho(x,t) = (4\pi/\varepsilon)\Sigma_i z_i c_i(x,t), \tag{3}$$

where $f_i(x,t)$ and $c_i(x,t)$ are the flux and concentration of defect i at position x and time t, respectively. D_i and z_i are the diffusion coefficient and valence of defect i, respectively. $E(x,t)$ and $\rho(x,t)$ are the electric field and the charge density at position x and time t, respectively. F, R, T, and ε are the Faraday constant, the gas constant, the absolute temperature, and the dielectric permittivity, respectively. The Poisson equation (Eq. (3)) is replaced by the expression of the displacement current equation for convenience, resulting in the following equation,

$$I = F\Sigma_i z_i f_i(x,t) + (\varepsilon/4\pi)\partial E(x,t)/\partial t, \tag{4}$$

where I is the total current density, which is a setting parameter in the PoNPs code. The electric potential $\phi(x,t)$ at position x and time t vs. that at $x = 0$ is given by

$$\phi(x,t) = -\int_{[0,x]} E(x,t)\mathrm{d}x. \tag{5}$$

As for the second term on the right hand of Eq. (2), i.e., intra-layer reaction term, an intra-layer reaction r is expressed by set α_r of stoichiometric coefficients of all defect $\{\alpha_{ir}\}$ ($i = 1, \ldots, n_{\mathrm{def}}$), where n_{def} is the number of defect species. In the present definition, reactants have a *negative* stoichiometric coefficient, while products have a *positive* coefficient. The reaction rate is assumed to be proportional to the Gibbs energy change of the reaction r, ΔG_r, under the linear response approximation, expressed as follows:

$$[\partial c_i(x,t)/\partial t]_r = -\alpha_{ir} k_{\mathrm{intra},r}\Delta G_r/RT = -\alpha_{ir} k_{\mathrm{intra},r}\,\Sigma_i \alpha_{ir}\widetilde{\mu}_i(x,t)\,/\,RT$$

$$= -\alpha_{ir} k_{\mathrm{intra},r}\,(\,\Delta G^0_r + \Sigma_i \alpha_{ir}(\,RT\ln(c_i(x,t)/[\mathrm{mol/cm}^3]) + z_i F\phi(x,t)\,)\,)\,/\,RT, \tag{6}$$

$$(R: \mathrm{J/mol\cdot K},\ T: \mathrm{K},\ \Delta G^0_r: \mathrm{J/mol},\ c_i: \mathrm{mol/cm}^3,\ k_{\mathrm{intra},r}: \mathrm{mol/cm}^3\cdot\mathrm{s})$$

where $k_{\mathrm{intra},r}$ is the reaction rate, $\widetilde{\mu}_i$ is the electrochemical potential of defect i. ΔG^0_r is the standard Gibbs energy change of reaction r, which is specified in ***kJ/mol*** in reaction.csv. For an intra-layer reaction, the electrochemical potential is equal to the chemical potential, because the reaction proceeds within single space elements at the same electric potential $\phi(x,t)$.

For an inter-layer reaction, the reactants and products can exist in the left and right layers to the interface position x_j. Therefore, the stoichiometric coefficients should be defined for the left and right layers, l_j and l_{j+1}, which are given as $\alpha_{lr} = \{\alpha_{ilr}\}$ ($i = 1, \ldots, n_{\mathrm{def}}$, $l = l_j, l_{j+1}$). As a result, the flux of defect i by reaction r at position x_j on the layer l side, f_{ijlr}, is given by a similar equation to Eq. (6),

$$f_{ijlr}(x,t) = -\alpha_{iljr} k_{\mathrm{inter},r}\,(\,\Delta G^0_r + \Sigma_{i,\,j'=j,j+1}\alpha_{ilj'r}(\,RT\ln(c_{ij'}/[\mathrm{mol/cm}^3]) + z_i F\phi_{j'}\,)\,)\,/\,RT. \tag{7}$$

Note that the unit of $k_{\mathrm{inter},r}$ (***mol/cm²·s***) is different from that of $k_{\mathrm{intra},r}$ (***mol/cm³·s***).

Space grid and variable definitions

In the PoNPs code, Eqs. (1), (2), and (4) are solved numerically by discretizing the space and time. Since the defect concentrations and electric fields can drastically change near hetero-interfaces, the space grid should be fine near both ends of each layer and rough for the bulk region. When the space grid in layer j is automatically generated, an arithmetic sequence is used for the interface regions up to several times of the Debye length in layer j (*n_ldebye* times of $\lambda_{D,j}$). $\lambda_{D,j}$ is given by $(\varepsilon_j RT/F^2)/\Sigma_i z_i^2 c_{ij,ave}$, where $c_{ij,ave}$ is the average concentration of defect i in layer j. The Debye length is furthermore divided by several pieces (*n_elem_ldebye* pieces) in the PoNPs code. On the other hand, a geometric sequence is used for the bulk region, where the geometric ratio is automatically determined by specifying the length of the layer and the number of space grid in the layer. As an example, the space grid is shown in Fig. 2 when the total number of space elements N is set to be 13 with a single layer, *n_elem_ldebye* = 2, and *n_ldebye* = 2. The defect concentration is defined at the middle of each space element as the average concentration in the space element. The defect concentrations at both ends are defined as c_0 and c_{N+1} corresponding to the reservoirs concentrations c_L and c_R, respectively. On the other hand, the flux f_i of defect i, the electric potential ϕ, and the electric field E are defined on the boundaries of adjacent space elements.
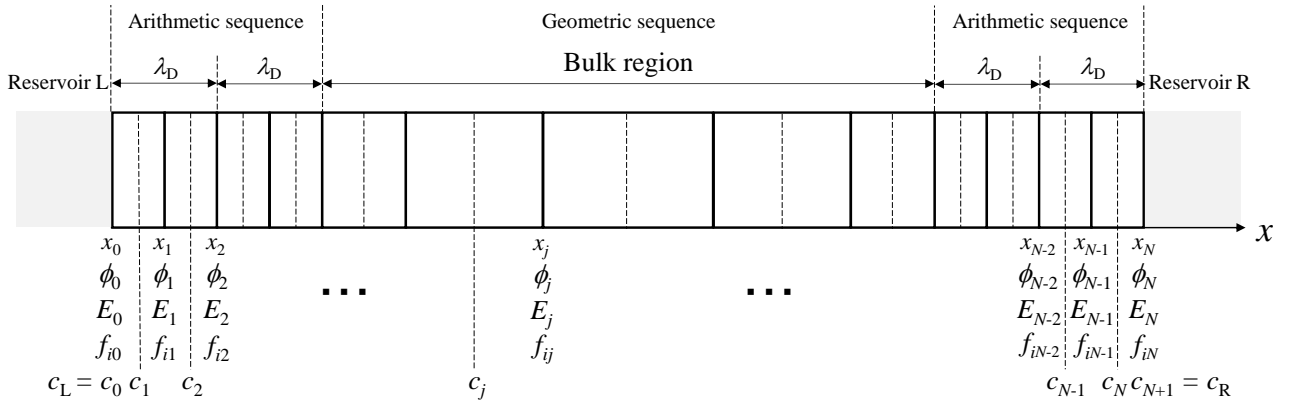

Fig. 2. Schematic drawing of the space grid and the variable definitions when the total number of space elements is set to be 13 with a single layer, *n_elem_ldebye* = 2, and *n_ldebye* = 2.

Time grid

There are several relaxation processes in PNP systems with multiple mobile defect species, whose time constants generally cover over a wide range. Therefore, a geometric sequence is used in the automatic generation of the time grid in this code. τ_∞ denotes the smallest time constant, given by $\min_j (\varepsilon_j RT/F^2)/\Sigma z_i^2 D_{ij} c_{ij,\text{ave}}$, where ε_j and D_{ij} are the dielectric permittivity and the diffusion coefficient of defect i in layer j, respectively. τ_∞ is governed by the fastest defects in a given system. On the other hand, the largest time constant is governed by the slowest defects, which is called *Debye time*, τ_D. τ_D is given by $\max_j d_j^2/D_{\text{slow},j}$, where d_j and $D_{\text{slow},j}$ is the distance of layer j and the slowest diffusion coefficient in the layer, respectively. In this program, the geometric time grid from $\tau_\infty/100$ to τ_D are automatically generated at *mkTimeGrid* = auto.

Solution of PNP equations

In the PoNPs code, the time evolution of concentration and electric field profiles governed by Eqs. (1),(2), and (4) is simulated by the Newton-Raphson (NR) method. See the following reference in details. The stopping criteria of the NR iterations are based on the change rates of concentrations and electric fields. The thresholds are specified in comp.csv. Sometimes, the stopping criteria are not satisfied even if the concentration and electric field profiles correctly converge, e.g., some concentrations and electric field are almost zero. In such a case, the convergence conditions can be switched to the criterion based on the change in total voltage between both ends.

Ref. T. R. Brumleve and R. P. Buck, Numerical solution of the Nernst-Planck and Poisson equation system with applications to membrane electrochemistry and solid state physics, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **90**, 1-31 (1978).

Impedance spectroscopy

In the PoNPs code, the concentration profiles of defect species and electric field profiles in the steady state should be prepared, prior to impedance simulations. Impedance simulations in this code are equivalent to the time evolution simulation with a small perturbation current δI. The impedance $Z(\omega)^* = Z_{\text{re}}(\omega) + iZ_{\text{im}}(\omega)$ can therefore be estimated by Fourier transformation of the voltage-time response to the perturbation. Using cell voltage $V^*(\omega) = V_{\text{re}}(\omega) + iV_{\text{im}}(\omega)$, the impedance is given by

$$Z_{\text{re}}(\omega) = -V_{\text{im}}(\omega)\, \omega / \delta I, \tag{8}$$

$$Z_{\text{im}}(\omega) = V_{\text{re}}(\omega)\, \omega / \delta I, \tag{9}$$

$$V_{\text{re}}(\omega) = \int_{[0,\infty]} (V(t) - V(\infty))\cos\omega t\, dt, \tag{10}$$

$$V_{\text{im}}(\omega) = -\int_{[0,\infty]} (V(t) - V(\infty))\sin\omega t\, dt - (V(\infty) - V(0)) / \omega. \tag{11}$$

The integral terms in $V_{\text{re}}(\omega)$ and $V_{\text{im}}(\omega)$ are considered as the summation of individual time intervals ΔV_k ($k = 1, \ldots,$ *n_timeSteps*) in the specified time grid, as follows:

$$V_{\text{re}}(\omega) = \Sigma_k \Delta V_{\text{re},k}, \tag{12}$$

$$\Delta V_{\text{re},k} = [(V(t_k) - V(t_{k-1}))/(t_k - t_{k-1})]\,[\cos\omega t_k - \cos\omega t_{k-1}] / \omega^2$$
$$+ [(V(t_k) - V(\infty))\sin\omega t_k - (V(t_{k-1}) - V(\infty))\sin\omega t_{k-1}] / \omega, \tag{13}$$

$$V_{\text{im}}(\omega) = \Sigma_k \Delta V_{\text{im},k} - (V(\infty) - V(0)) / \omega, \tag{14}$$

$$\Delta V_{\text{im},k} = [(V(t_k) - V(t_{k-1}))/(t_k - t_{k-1})]\,[\sin\omega t_k - \sin\omega t_{k-1}] / \omega^2$$
$$- [(V(t_k) - V(\infty))\cos\omega t_k - (V(t_{k-1}) - V(\infty))\cos\omega t_{k-1}] / \omega. \tag{15}$$

[Simulation examples]

<u>**Example01**</u>

Objective: A steady state under the open circuit condition ($I = 0$ A)

System: Single layer electrolyte (LYTE)

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h) (& immobile dopants)

      Thickness: 100 μm

      Number of space elements (*n_elem*): 101 or 201

      Left reservoir: fuel electrode (RES_L), Right reservoir (RES_R): air electrode

      Initial electric field: zero [V/cm] at all positions

      Initial defect concentration profiles: three types shown below:

Input1-*n_elem*:

      Initial defect concentrations: constant at c_L (same as the fuel electrode side)

      Not converge by the criteria based on the change rates in defect concentrations and electric field

      Converge successfully by using the criterion based on the change in cell voltage

Input2-*n_elem*:

      Initial defect concentrations: constant at c_R (same as the air electrode side)

      Using default setting, hole concentrations are zero at the first step, and the simulation is aborted.

      If the lower bound of hole concentration is set to 1.0E-20 in defect.csv, the same steady state as that of input1

      can be obtained.

Input 3-*n_elem*:

      Initial defect concentrations: Interpolated using c_L and c_R.

     The converged steady state is different from those by inputs1&2. The convergence depends on initial profiles!

<u>**Example02**</u>

Objective: A steady state under a constant current condition

System: Single layer electrolyte (LYTE)

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h)

      Thickness: 100 μm

      Number of space elements (*n_elem*): 101 or 201

      Left reservoir: fuel electrode (RES_L), Right reservoir: air electrode (RES_R)

Input1-*n_elem* (*n_elem*: 101): $I = 100$ mA

      Initial conditions: Use the steady states in Example01

Input2-*n_elem* (*n_elem*: 101, 201): I = 300 mA

      Initial conditions: Use the steady states in Example01

      In the case of *n_elem* = 101, several concentrations are zero, and the simulation is aborted.

Example03

Objective: Current interrupt measurement

System: Single layer electrolyte (LYTE)

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h)

      Thickness: 100 μm

      Number of space elements (*n_elem*): 101 or 201

      Left reservoir: fuel electrode (RES_L), Right reservoir: air electrode (RES_R)

Input 1-101: Initial conditions are same as Example02 input1-101 (I = 100 mA → 0 mA)

Input 2-201: Initial conditions are same as Example02 input2-201 (I = 300 mA → 0 mA)

Example04

Objective: Impedance spectroscopy (I = 0 or 100 mA, δI = 1 mA)

System: Single layer electrolyte (LYTE)

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h)

      Thickness: 100 μm

      Number of space elements (*n_elem*): 101

      Left reservoir: fuel electrode (RES_L), Right reservoir: air electrode (RES_R)

Input 1-101: Initial conditions are same as Example01 input1-101 (I = 0 mA, δI = 1 mA)

Input 2-101: Initial conditions are same as Example02 input1-101 (I = 100 mA, δI = 1 mA)

Example05

Objective: Impedance spectroscopy of symmetric cells (I = 0, δI = 1 mA)

System: Single layer electrolyte (LYTE)

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h)

      Thickness: 100 μm

      Number of space elements (*n_elem*): 101

      Reservoirs (RES_L,RES_R): fuel electrode or air electrode

Input 1-101: Symmetric cell of fuel electrodes

Input 2-101: Symmetric cell of air electrodes

Example06

Objective: A steady state and impedance spectroscopy in a two-layer cell with blocking layer

System: Electrolyte (LYTE) 100 μm / Blocking layer (BLK, hole concentration: 1 % vs. LYTE) 100 μm

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h)

      Number of space elements (*n_elem*): 101 for each layer

      Left reservoir: fuel electrode (RES_L), Right reservoir: air electrode (RES_R)

Input1: Open circuit condition (I = 0 mA)

Input2: Constant current condition (I = 100 mA)

Input3: Impedance spectroscopy under the open circuit condition (I = 0 mA, δI = 1 mA)

Input4: Impedance spectroscopy under the constant current condition (I = 100 mA, δI = 1 mA)

Example07

Objective: Symmetry cell of air electrodes under constant current conditions

SYSTEM: AIR/LYTE/AIR

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h) In LYTE

                Oxygen vacancy (VO), hole (h) In AIR

      Thickness: 50, 100, 50 μm

      Number of space elements (*n_elem*): 101 for each layer

Input1-4: Constant current (I): 0, 10, 50, 100 mA

Example08

Objective: Symmetry cell of fuel electrodes under constant current conditions

SYSTEM: FUEL/LYTE/FUEL

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h) in LYTE

                Proton (H), Oxygen vacancy (VO), electron (e) in FUEL

      Thickness: 50, 100, 50 μm

      Number of space elements (*n_elem*): 101, 201, 101

Input1-4: Constant current (I): 0, 10, 50, 100 mA

dt_max should be set to 1e+3.

Example09

Objective: Fuel cell under constant current conditions

SYSTEM: FUEL/LYTE/AIR

      Defect species: Proton (H), Oxygen vacancy (VO), hole (h) In LYTE

                Proton (H), Oxygen vacancy (VO), electron (e) in FUEL

                Oxygen vacancy (VO), hole (h) In AIR

      Thickness: 50, 100, 50 μm

      Number of space elements (*n_elem*): 101, 201, 101

Input1-4: Constant current (I): 0, 10, 50, 100 mA

dt_max should be set to 1e+3.

Setting parameters in examples:

Temperature: T = 773.15 K

Electrolyte (LYTE)

ε_r = 62, D_H = 5*10^{-7} cm^2/s, D_{VO} = 5*10^{-9} cm^2/s, D_{hole} = 1*10^{-6} cm^2/s

Blocking layer (BLK)

ε_r = 62, D_H = 5*10^{-7} cm^2/s, D_{VO} = 5*10^{-9} cm^2/s, D_{hole} = 1*10^{-6} cm^2/s

Fuel electrode (FUEL)

ε_r = 200, D_H = 1*10^{-7} cm^2/s, D_{VO} = 1*10^{-9} cm^2/s, D_e = 1*10^{-4} cm^2/s (gas diffusion: very fast)

Air electrode (AIR)

ε_r = 50, D_{VO} = 5*10^{-8} cm^2/s, D_{hole} = 1*10^{-6} cm^2/s (gas diffusion: nothing)

Reservoir (RES)

RES/LYTE: k_H = 1*10^{-6} mol/cm^{2}s, k_{VO} = 1*10^{-7} mol/cm^{2}s, k_{hole} = 1*10^{-3} mol/cm^{2}s

LYTE/BLK: k_H = 1*10^{-4} mol/cm^{2}s, k_{VO} = 1*10^{-4} mol/cm^{2}s, k_{hole} = 1*10^{-4} mol/cm^{2}s

RES/FUEL: k_H = 1*10^{-4} mol/cm^{2}s, k_{VO} = 1*10^{-5} mol/cm^{2}s, k_e = 1*10^{-1} mol/cm^{2}s

RES/AIR: k_{VO} = 1*10^{-5} mol/cm^{2}s, k_h = 1*10^{-1} mol/cm^{2}s

FUEL/LYTE: k_H = 1*10^{-6} mol/cm^{2}s, k_{VO} = 1*10^{-7} mol/cm^{2}s, $k_{e,h}$ = 1*10^{-3} mol/cm^{2}s

AIR/LYTE: $k_{VO,H}$ = 1*10^{-6} mol/cm^{2}s, k_{VO} = 1*10^{-7} mol/cm^{2}s, k_h = 1*10^{-3} mol/cm^{2}s

FUEL: $k_{H,e}$ = 1*10^{-2} mol/cm^{3}s, $k_{VO,e}$ = 1*10^{-2} mol/cm^{3}s