ENBIOS-1D Lab v.3.0 User Guide – v3.0_2017.04.13

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New with respect to previous version

Version 3.0 of ENBIOS-1D Lab includes the following new features with respect to previous versions:

0) Revised User Guide (this file) and Numerical examples file
1) Option to add a thin dielectric layer to model the Stern layer between the insulator and the electrolyte (Compact Layer)
2) Revised default options concerning the activation of DC and AC site-binding charge density
3) Four pH-determining salts: HCl and HNO_3 (strong acids), NaOH and KOH (strong bases)
4) Space charge density plot in both the semiconductor and electrolyte regions
5) Restyling of a few menus and bug fixes

Version 2.0 of ENBIOS-1D Lab includes the following new features with respect to previous versions:

0) This documentation (User Guide) and examples (Numerical examples)
1) New Electrode/Electrolyte/Electrode structure
2) AC small signal site binding charge added to the DC one for admittance simulations
3) Custom electrolyte option
4) Temperature dependent intrinsic concentration in semiconductors
5) Improved plotting algorithm to avoid the generation of spurious zeros in the AC response
6) User defined convergence threshold
7) Restyling of a few menus and bug fixes

Introduction

ENBIOS-1D Lab is a tool to simulate simple structures comprising electrolytes, insulators and semiconductor in one dimension. It is meant for use as a teaching tool in support of undergraduate or graduate courses on the basic physics of transduction in ion and particle sensors, and to assist early stage researchers getting familiar with some basic concepts in the field.

At present, the Rappture interface of ENBIOS-1D Lab supports parameters' input (left quadrant), simulation, and visualization (right quadrant) of impedance/admittance spectra as well as DC and AC potential, ion and charge carrier concentration in simple one-dimensional Electrolyte, (E) Electrolyte/Insulator (EI) and Electrolyte/Insulator/Semiconductor (EIS) systems. Figure 0 shows all these structures. A 2D version of the tool (ENBIOS-2D Lab) is available on nanoHUB to simulate Ion Sensitive Field Effect Transistor (ISFET). A broader set of case studies may become available with future releases of the tool, possibly including Interdigitated structures and Nanoelectrode array devices; please give us your feedback on the most useful updates and case studies.
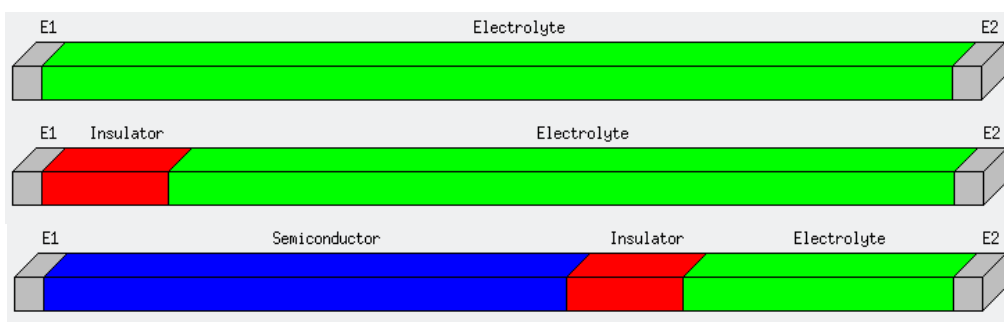

Figure 0: Schematic representation of the Electrolyte, Electrolyte/Insulator and Electrolyte/Insulator/Semiconductor systems in ENBIOS-1D Lab. The Compact Layer added as of version 3.0 of the tool is not shown.

ENBIOS-1D Lab is powered by ENBIOS, (Electronic Nano-BIOsensor Simulator), a general purpose three-dimensional Control Volume Finite Element Method (CVFEM) simulator developed in-house at the University of Udine – Italy [Pittino2014]. ENBIOS simulates in three dimensions (3D) the DC and AC small signal impedance response to ions and micro/nanoparticles of three-dimensional devices made of semiconductor, insulator and electrolyte materials. If you are interested in this kind of more complete simulations please contact luca.selmi@uniud.it via nanoHUB.

A simple example to start with

Try running a few simple simulations to get acquainted with ENBIOS-1D Lab. Start the tool and select the Electrolyte/Insulator system in the "Structure" menu at the top. The "Device" folder shows the image of the structure at the bottom. Now click on the "Electrodes" folder to decide the type of contact to the electrolyte via the E2 electrode. ENBIOS-1D Lab supports two types of contacts: Faradaic and Ideally-polarizable. A precise definition of both types of electrodes is given in the following section "Boundary conditions". At this stage, it is sufficient to know that in the EI structure a Faradaic contact sets the bulk electrolyte potential and impedes the formation of space charge layers at the electrode. In other words, this choice enforces charge neutrality at the contact in both DC and AC conditions.

Click on the "Insulator(s)" folder (Figure 1). You can the select the insulator material and thickness, e.g., SiO_2 and the default value of 3 nm. You can also turn on and off the calculation of the DC and AC site-binding charge generated at the electrolyte/insulator interface by the protonation/deprotonation reactions of the oxidril surface sites [Yates1974]. For a first trial, you may want to keep the site-binding charge option switched off and just observe the values of the insulator physical constants below the thickness box. As of version 3.0 it is also possible to explicitly include an additional insulating layer between the insulator and the electrolyte regions (not shown in Figure 0) to model the so-called Stern layer of absorbed ions at the interface. User defined parameters of the compact layer are the thickness, the relative permittivity and the surface charge; the latter is located at the interface between the compact layer and the electrolyte. Note that if both DC site-binding charge and compact layer are enabled, the site-binding charge will be placed at the insulator/compact layer interface (see "Compact layer" section for more details). We will not use the compact layer in this first sample simulation.
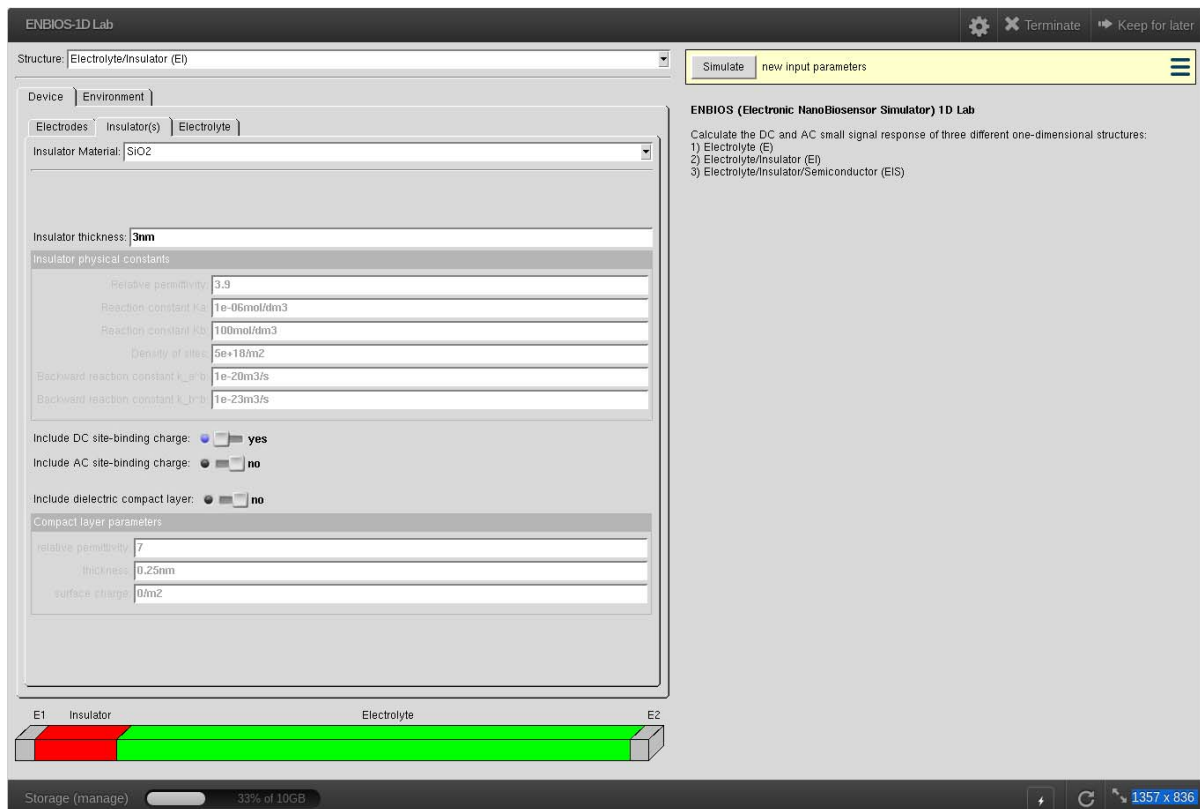

Figure 1: "Device/Insulator(s)" folder of the Rappture interface for the Electrolyte/Insulator system.
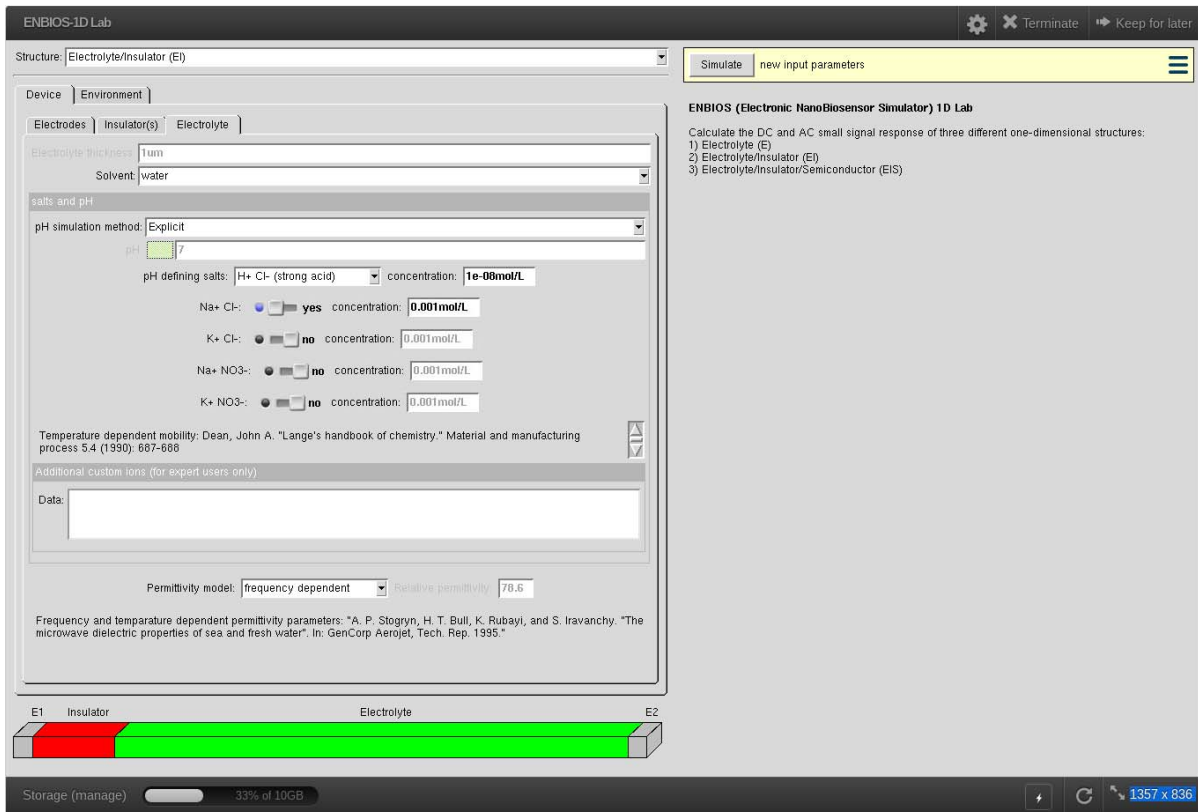
Figure 2: "Device/Electrolyte" folder of the Rappture interface for the Electrolyte/Insulator system.
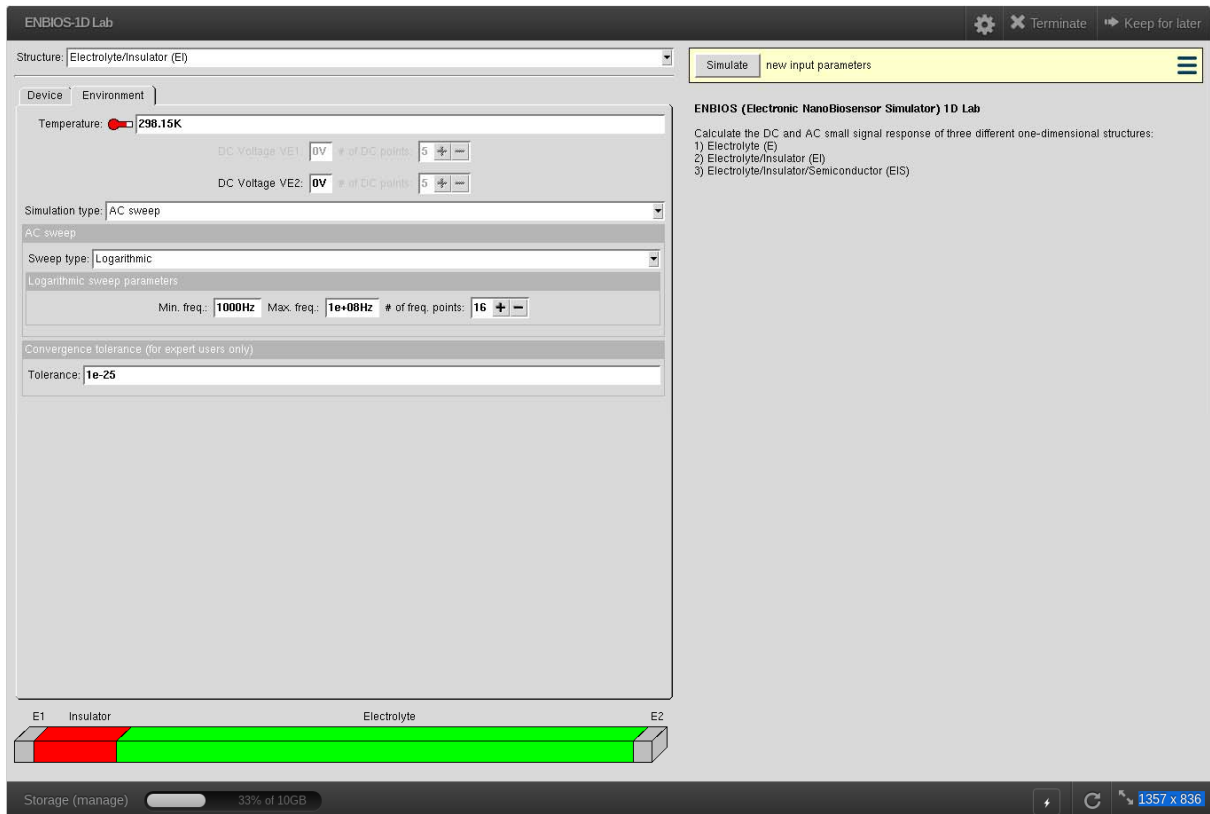

Figure 3: "Environment" folder of the Rappture interface for the Electrolyte/Insulator system.

You can then move to the "Electrolyte" folder (Figure 2). Here you can start setting the pH of the electrolyte. The simplest way to do it is to choose the "implicit" pH simulation method option, set the pH

value (let's start with pH=7) and decide the concentration of the available salts. If you choose "explicit pH simulation method" then you will have to decide which acid or base sets the pH and give its concentration. Anything between 1 and 100 mM will be OK for a first run although the interface accepts values in a much larger range. We will use 1 mM NaCl in this example. This Folder also lets users choose among models for the electrolyte complex permittivity (scroll down the folder if this is not immediately visible), as explained in the "Physics" section below. The default choice (frequency dependent) is the most complete and accurate; for this example, however, change it to a constant permittivity value of 78.6.

You are now ready to switch to the "Environment" folder (Figure 3) where the temperature and the parameters of the DC bias voltage sweep at the E2 electrode become accessible. Try for instance V_{E2} = 0.2 V and 5 bias steps to start with. ENBIOS-1D Lab will calculate all DC bias points up to the final voltage and then run an AC small signal simulation at all frequencies specified by the remaining fields of this folder (linear or logarithmic sweep, etc…). Increase the number of frequency points to, e.g., 20 to get smoother curves. ENBIOS uses a fixed signal amplitude of 1mV for calculations in the AC regime.

Now press the "Simulate" pushbutton and wait for nanohub to show the results in the right panel of the Rappture interface. You can follow the progress of the simulation via short textual updates. Among them ENBIOS displays the electrolyte Debye length λ_D, a useful value to define an optimized simulation mesh, and the DC electrolyte permittivity. The meshing algorithms seek for a reasonable compromise between speed and accuracy and still exhibit some limitations, especially in the determination of phase at the highest frequencies. ENBIOS-1D Lab may take several seconds past the end of the simulation before the output plot panel appears, because it has to save a large amount of data for later display.

The "Results" menu shows this clearly (Figure 4). Potential and ion concentrations are available as a function of position at all DC bias points and for the last DC bias in the AC regime. Furthermore, you can display impedance and admittance data versus frequency for the last bias point in a large number of equivalent formats. Staying on the default "Potential (DC)" option and pressing the "Play" pushbutton at the bottom left of the panel (red oval in Figure 4) you will see E2 voltage increase at the contact and in the bulk of the electrolyte, while a potential drop develops in the insulator and in the electrolyte diffused layer. You can for instance zoom-in the interface region and observe the exponential decay of the potential in the electrolyte and the linear potential in the neutral insulator (Figure 5a, green oval). Change the graph to "Ion concentrations (DC)" and click "play" again. At the highest bias, point you will note the accumulation of Na^+ ions and the depletion of Cl^- ions over approximately the first 50 nm from the interface next to E1, that is, the electrode at the lowest potential. As of version 3.0 the H^+ and OH^- concentrations are shown as well.

Now try to select the "Potential (AC-Real and Imaginary)" option. You can "Play" and observe the AC potential change as a function of frequency. At low frequency, the AC potential drops almost entirely at the electrolyte/insulator interface (orange oval, Figure 5b); this is the AC electrical double layer. As frequency increases ions do not respond to the rapidly varying AC signal and the electrolyte tends to behave as an insulator. The AC voltage drop over the AC electrical double layer diminishes and the potential over most of the electrolyte becomes a linear function of distance (see zoom in the blue oval of Figure 5c). Eventually, at frequency much larger than the electrolyte dielectric relaxation cut-off frequency $f_2 = 1/(2\pi\varepsilon_{el}/\sigma_{el})$ the potential in the electrolyte is perfectly linear, as expected for an ideal insulator. The admittance between electrodes is shown in Figure 5d. The observed trends can be interpreted as the result of the series connection of the insulator capacitance, C_{ox}, the electrical double layer capacitance, C_{edl}, and the parallel connection of the solution resistance, R_{sol}, and capacitance, C_{sol}, as illustrated in Figure 6. Note that the equivalent circuit of Figure 6 with parameter values taken from the geometry of the sample and electrical double layer thickness is only accurate if $\lambda_D \ll T_{el}$.

This example illustrates the principle of high frequency impedance spectroscopy, whereby a high frequency signal is used to establish an AC field deep in the electrolyte, thus overcoming the Debye screening limit and enabling the detection of analytes at distances beyond λ_D. In fact, analytes in the bulk of the electrolyte affect the AC field distribution and change the charge on the electrode, that is, the electrode admittance.

This simple example should be sufficient to get familiar with the basic functions of ENBIOS-1D Lab. More complete and quantitative exercises are discussed in the document "Numerical Examples".
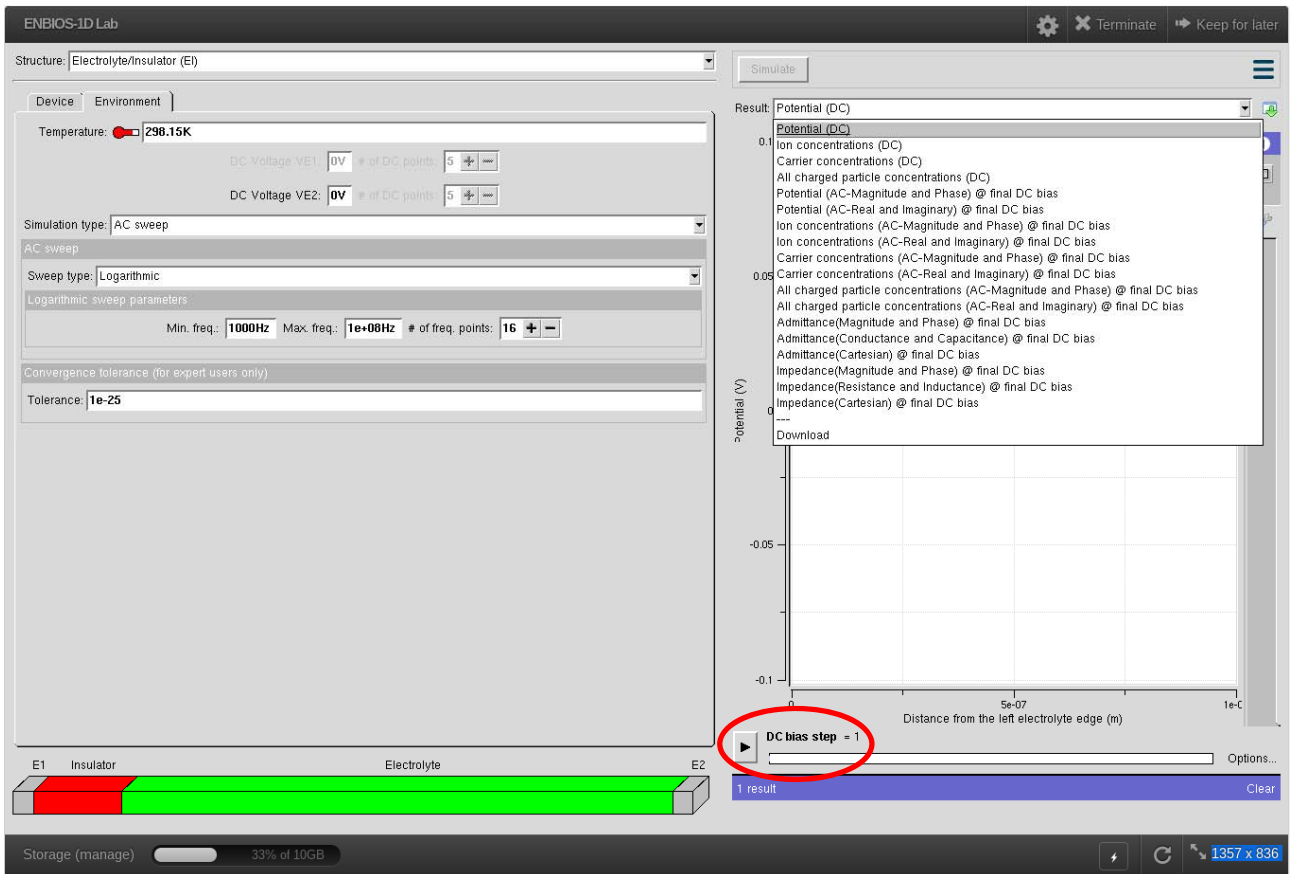
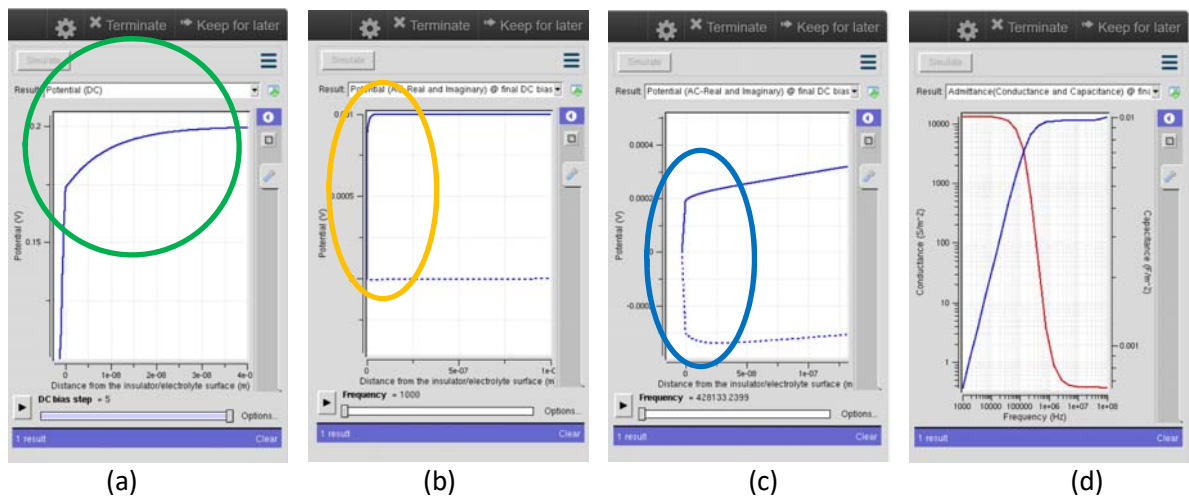Figure 4: "Result" options' menu of the Rappture interface.

(a) (b) (c) (d)

Figure 5: (a) DC potential of the Electrolyte/Insulator system at V_{E2}=0.2V; the corresponding AC potential at 1000 Hz and 428 kHz is shown in real and imaginary parts in graphs (b) and (c), respectively. Graph (d) shows the conductance and capacitance as a function of frequency.
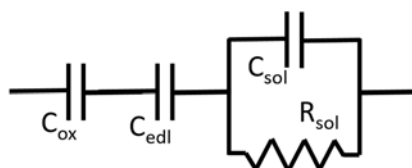

Figure 6: Lumped elements AC small signal equivalent circuit of the Electrolyte/Insulator system.

Model equations in ENBIOS

In DC operation the **electrolyte** is modelled with the Poisson-Boltzmann (PB) equation. It reads:

$$\nabla \cdot (\varepsilon \nabla V_0) = -\left(\rho_f + \sum_{m=1}^{N_{sp}} Z_m q n_m^\infty \exp\left(\frac{Z_m q}{k_B T} (\phi_{0m} - V_0) \right) \right)$$

where V_0 is the DC potential, ρ_f the fixed charge, N_{sp} the number of ion species, Z_m the signed ion valence and the m-th ion concentration is given by

$$n_m = n_m^\infty \exp\left(\frac{Z_m q}{k_B T} (\phi_m - V) \right)$$

Φ_m being the ion quasi-potential and n_m^∞ the ion concentration at the point where $\Phi_m = V$. Since the PB equation entails equilibrium, no gradient of the ion quasi-potentials can exist in the electrolyte. ENBIOS-1D Lab sets the Φ_{0m} to the same constant value, denoted V_{ref}, for all ion species. If not otherwise defined by the boundary conditions V_{ref} is set to zero volts.

The well-known drift-diffusion model describes the **semiconductor**. The model equations will not be repeated here since they are common to any microelectronic TCAD environment. We assume users are familiar with them. In ENBIOS the semiconductor mobility is constant, Einstein relation holds between mobility and diffusivity, and generation-recombination terms are zero. Note that at the time of writing, ENBIOS supports the calculation of DC currents only through the semiconductor, not through the electrolyte.

In AC operation the linearized Poisson/Nernst/Planck - Poisson/Drift/Diffusion equations apply to both the semiconductor and the electrolyte. Assuming all physical quantities are time-harmonic functions of the form

$$\phi_m = \phi_{0m} + \Re\left[\tilde{\phi}_m \exp(j\omega t) \right]$$
$$V = V_0 + \Re\left[\tilde{V} \exp(j\omega t) \right]$$

and the only time varying charges are those of the electrolyte ions (no site-binding charge) we obtain

$$\nabla \cdot \left(\varepsilon \nabla \tilde{V} \right) + \sum_{m=1}^{N_{sp}} \frac{Z_m^2 q^2}{k_B T} n_{0m} \left(\tilde{\phi}_m - \tilde{V} \right) = 0$$

$$Z_m q \mu_m \nabla \cdot \left(n_{0m} \left(\frac{Z_m q}{k_B T} \left(\tilde{\phi}_m - \tilde{V} \right) \nabla \phi_{0m} + \nabla \tilde{\phi}_m \right) \right) - j\omega n_{0m} \frac{Z_m q}{k_B T} \left(\tilde{\phi}_m - \tilde{V} \right) = 0$$

$$\tilde{n}_m = n_{0m} \frac{Z_m q}{k_B T} \left(\tilde{\phi}_m - \tilde{V} \right)$$

The ions' transport equations in the electrolyte are further simplified by reminding that all the DC ion quasi-potentials, Φ_{0m}, are constant and equal to the potential V_{ref}. Consequently, the term proportional to the gradient of Φ_{0m} is zero. If not otherwise defined by the DC boundary conditions ENBIOS sets $V_{ref} = 0V$ for AC analysis.

Boundary conditions in ENBIOS

ENBIOS boundary conditions are of the Dirichlet or Neumann type for the electrostatic potential, the ion quasi-potentials and the carrier concentrations. In general terms, for **the DC analysis** we have:

$$\begin{cases} V_0 = V^D & \text{on } \Gamma_D^V \\ \phi_{0m} = \phi_m^D & \text{on } \Gamma_D^\phi \\ \varepsilon \nabla V_0 \cdot \hat{n} = 0 & \text{on } \Gamma_N^V \\ \nabla \phi_{0m} \cdot \hat{n} = 0 & \text{on } \Gamma_N^\phi \end{cases}$$

where Γ_D^V, Γ_N^V are the Dirichlet and Neumann boundaries for the potential, respectively, V^D and $\Phi_m{}^D$ are the potential and ion quasi-potential values at the Dirichlet boundary (similar definitions apply to Φ_m).
The boundary conditions for **the AC analysis** are of the form:

$$\begin{cases} \tilde{V} = \tilde{V}^D & \text{on } \tilde{\Gamma}_D^V \\ \tilde{\phi}_m = \tilde{\phi}_m^D & \text{on } \tilde{\Gamma}_D^\phi \\ \varepsilon \nabla \tilde{V} \cdot \hat{n} = 0 & \text{on } \tilde{\Gamma}_N^V \\ \vec{\tilde{J}}_m \cdot \hat{n} = 0 & \text{on } \tilde{\Gamma}_N^\phi \end{cases}$$

where $\tilde{J}_m$ is the m-th ion species AC current density. The conditions above show that in principle ENBIOS can set the following quantities for each electrode: V^D and $\tilde{V}^D$, $\Phi_m{}^D$ and $\tilde{\Phi}_m{}^D$.

These boundary conditions allow ENBIOS to emulate two types of contacts to the electrolyte (and the semiconductor):

- Faradaic (Ohmic) boundaries are of type Dirichlet for both V and Φ;
- Ideally-polarizable (Floating) boundaries are of type Dirichlet for V and Neumann for Φ;.

Faradaic (Ohmic) contacts mimic contacts that support electrochemical reactions (generation-recombination processes, respectively); therefore, non-zero ionic (electron and hole) DC currents can flow through these electrodes. Faradaic contacts do not create electrical double layers, regardless of their bias voltage.

Ideally-polarizable (Floating) contacts are blocking contacts; DC ionic currents (electron and hole currents) are zero, and only displacement currents are possible at these contacts. Ideally-polarizable contacts generate an electrical double layer in the electrolyte unless their bias voltage is equal to V_{ref}.

In the DC regime, at most one Faradaic electrode must be in contact to the **electrolyte region**. If all contacts to the electrolyte are defined as Ideally-polarizable (i.e., no Faradaic contacts to the electrolyte), then ENBIOS sets $\Phi_{0m} = \Phi_m{}^D = V_{ref} = 0V$ for all ions. If there is one Faradaic contact, then the DC bias at that electrode is taken as V_{ref} and all ion quasi-potentials are set equal to such V_{ref}. If two or more contacts to the electrolyte are set to Faradaic, then the simulation stops with an error message. The $\Phi_m{}^D$ of Ideally-polarizable contacts is set to the applied bias voltage. If this latter is different from the reference potential, then the surface ion concentration will not be equal to the bulk value and an electrical double layer will form, as expected. As regards the **semiconductor region**, Faradaic contacts behave as Ohmic, and the following equations apply in DC:

$$n_1^D - n_2^D = N_D - N_A, \quad n_1^D n_2^D = n_i^2$$

$$\phi_1^D = \phi_2^D = \phi_F$$

where 1 stands for electrons, 2 for holes, N_A and N_D denote the acceptor and donor concentrations and the Fermi potential Φ_F equals the DC voltage at the electrode.

In the AC regime there is no difference in the way ENBIOS treats contacts to the semiconductor and the electrolyte. If the contact is Faradaic (Ohmic), then Dirichlet boundary conditions apply to both the potential and quasi-potentials. The small signal amplitude is set to $\tilde{V}^D$=1mV and $\tilde{V}^D = \tilde{\Phi}_m{}^D$ is imposed; consequently no AC double layer forms at the interface. If the contact is Ideally-polarizable, then ENBIOS sets Dirichlet boundary condtions on $\tilde{V}$ and Neumann ones on $\tilde{\Phi}_m$ and the formation of an AC double layer is obtained.

Contacts in ENBIOS-1D Lab

ENBIOS-1D Lab solves simple one dimensional structures with two contacts at the extremes. One of them (E2) is always in touch with the electrolyte. The other one (E1) contacts the other side of the electrolyte or the insulator or the semiconductor in the E, EI, and EIS structures, respectively. The contacts can be either Faradaic or Ideally-polarizable. Users can perform bias sweeps at one or more electrodes but at most one of those in contact with the electrolyte can be Faradaic in the E structure. In fact, two Faradaic contacts to the electrolyte set at different voltages would cause DC currents, but the PB equation used to describe the electrolyte does not account for them; thus, an inconsistency would be generated. ENBIOS-1D Lab automatically sets the electrolyte V_{ref} equal to the voltage at the electrolyte Faradaic contact, if existing. Otherwise, V_{ref} is set to zero V.

Physics

Semiconductor

ENBIOS-1D Lab implements a constant **carrier mobility**, defined as ratio between velocity and field. The **electrical permittivity** is also constant. The default values are listed in the "Semiconductor" folder. As regards the i**ntrinsinc carrier concentration**, the "Semiconductor" folder shows the value at the default temperature of 298.15 K (25 °C). The temperature dependence of n_i for Silicon and Germanium is described with the model in [Sze1981] with paramenters from [Joffe] (see Figure 7). The n_i values at the temperature set in the "Environment" folder are calculated at the start of each simulation; hence, they do not show up in the "Semiconductor" folder. In case "custom" semiconductor is chosen, the simulator always uses the semiconductor parameter values as they are defined in the "Semiconductor" folder; no additional calculation is done.
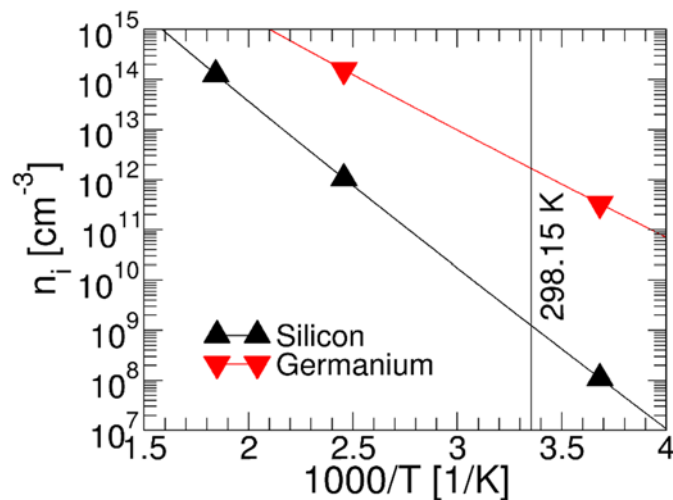

Figure 7: Intrinsic carrier concentration as a function of temperature after [Sze1981] and [Joffe].

Electrolyte

The **ionic strength and pH** of the electrolyte can be set by choosing the concentrations of a few predefined salts, acids and bases. Complete dissociation of all species is assumed in this case. Alternatively, the "user-defined" electrolyte option allows users to input the electrolyte composition in table form; ion valence and mobility should be given as well in the table (see popup window for the format). On-line pH calculators (e.g. aqion) can help finding the correct concentrations to input in the table. Note that ion concentrations should result in charge neutrality in the bulk electrolyte.

There are two ways to set the pH of the solution:

1) The "implicit pH" option excludes the possibility to choose predefined acids and bases, and adds H^+ and OH^- ions to the chosen salts when the site-binding charge is enabled (see "insulator" section). Note that this simple way to set the pH of the electrolyte independently of the salts respects charge neutrality, but it does not reflect the real

physics/chemistry of the solution; thus, it should be used with caution. For more details on this implementation see Appendix A.

2) The "explicit pH" option calculates the exact concentration of H+ and OH- ions depending on the chosen acids/bases composition, assuming complete dissociation and imposing charge neutrality. An example is reported in Appendix B.

ENBIOS defines the **ion mobility** as the ratio between velocity and force. International units of measure are chosen consistently. The ENBIOS default values at the default T=25 $^{\circ}$C are listed in Table 1.

	Na$^+$	K$^+$	Cl$^-$	NO3^{--}	H$^+$	OH$^-$
Mobility [10^{11} m/Ns]	3.242	4.755	5.052	4.620	22.648	12.809

Table 1: Ion mobility at the default temperature of 298.15 K.

The temperature dependence of the mobility is described via a polynomial interpolation of mobility data at 0, 18 and 25 $^{\circ}$C as available in [Dean1999]. Figure 8 reports the resulting ion mobility curves in ENBIOS.
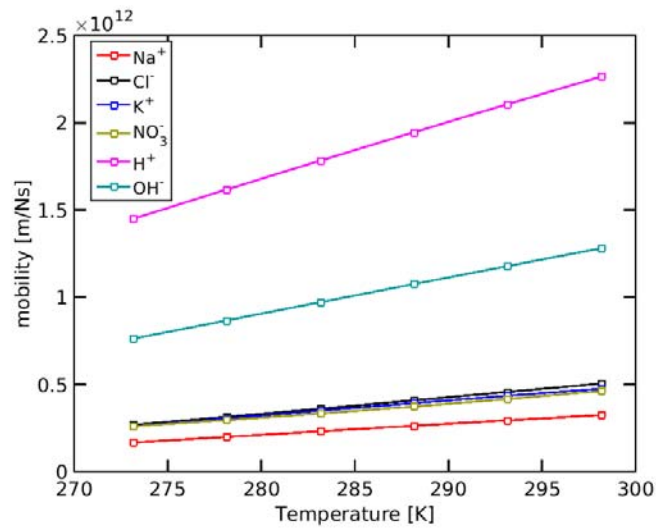

Figure 8: Ion mobility versus temperature currently implemented in ENBIOS.

ENBIOS implements a dedicated model for the frequency, temperature and salinity dependence of the **electrolyte electrical permittivity** with water solvent [Stogryn1995]. The model equation is

$$\varepsilon_{el} = \varepsilon_0 \left(\varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_1}{1 + j\omega\tau_{e1}} + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + j\omega\tau_{e2}} \right)$$

where the parameters are functions of salinity and temperature [Stogryn1995,Meissner2004] and take the following values at 298.15 K: ε_∞=4.5150, ε_s=78.3819, ε_1=6.1687, τ_1=8.3629e-12 s, τ_2=9.9949e-13 s. Figure 9 illustrates the salinity, temperature and frequency dependence of the electrolyte permittivity. The suggested range of simulation temperatures is restricted from 0 $^{\circ}$C to 50 $^{\circ}$C to avoid using the model beyond its range of calibrated validity.
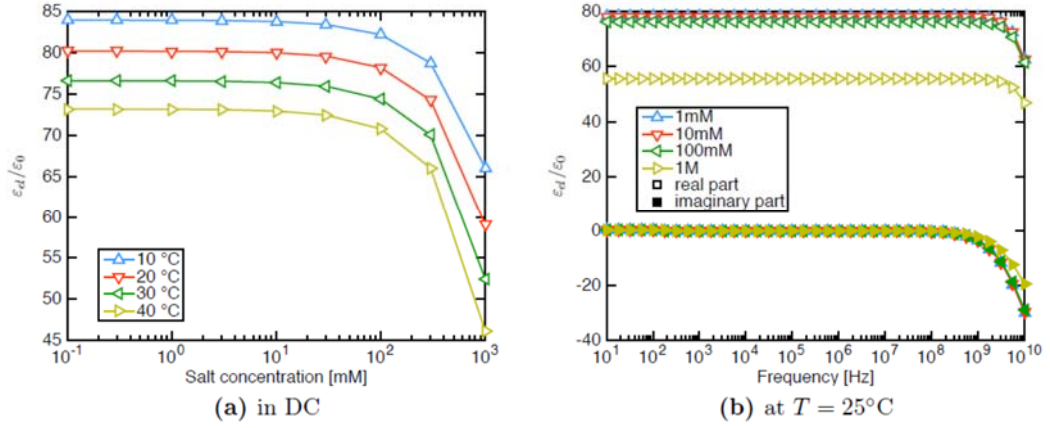
Figure 9: Salt concentration, temperature and frequency dependence of the electrolyte permittivity

Insulator

ENBIOS implements a constant **electrical permittivity** of the insulators. Default values are given in Table 2. Furthermore, ENBIOS can account for the build-up of a **site-binding charge** due to protonation and deprotonation reactions of the oxidril groups at the Electrolyte/Insulator interface [Yates1974]. The site-binding reactions are:

$$SiOH \overset{K_A}{\rightleftharpoons} SiO^- + H^+$$

$$SiOH_2^+ \overset{K_B}{\rightleftharpoons} SiOH + H^+$$
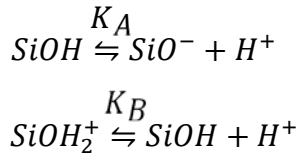
where K_A and K_B are the equilibrium reaction constants. In the DC regime, the surface charge can be expressed as:

$$\sigma_{sb} = qN_S \frac{n_{0Hs}^2 - K_a' K_b'}{n_{0Hs}^2 + K_b' n_{0Hs} + K_a' K_b'}$$

where $n_{0H_s} = n_{0H}^\infty \cdot exp\left(-\frac{qV_s}{k_B T}\right)$ is the surface concentration of H$^+$ ions that depends on V$_s$, the insulator surface potential with the electrolyte or with the compact layer if it is present (see "Compact layer" section for more details). N$_S$ is the surface density of binding sites and K$_A'$ and K$_B'$ are the equilibrium reaction constants of the site-binding reactions in m^{-3}. The parameters' values are listed in Table 2 and are available by default in the relevant menu.

	SiO$_2$	HfO$_2$	Al$_2$O$_3$	Ta$_2$O$_5$
Relative permittivity	3.9	25	9	22
Equilibrium K$_A$ [mol/l]	$1 \cdot 10^{-6}$	$1 \cdot 10^{-7}$	$1 \cdot 10^{-10}$	$1 \cdot 10^{-4}$
Equilibrium K$_B$ [mol/l]	$1 \cdot 10^2$	$1 \cdot 10^{-7}$	$1 \cdot 10^{-8}$	$1 \cdot 10^{-2}$
Backward reaction constant k$_A$^{b} [m^3/s]	$1 \cdot 10^{-20}$	n.a.	n.a.	n.a.
Backward reaction constant k$_B$^{b} [m^3/s]	$1 \cdot 10^{-23}$	n.a.	n.a.	n.a.
Surface density of binding sites [#/m^2]	$5 \cdot 10^{18}$	$1 \cdot 10^{19}$	$8 \cdot 10^{18}$	$1 \cdot 10^{19}$

Table 2: Site binding charge model parameters. At the time of writing the backward reaction constants for AC simulations of the site binding charge are implemented only for SiO$_2$.

Note that a "Custom insulator" option is also available to allow users create their own insulator and specify the relative static permittivity (ε_s, see above), the equilibrium reaction constants of the site-binding surface reactions (K_A, K_B) and the surface density of binding sites, N$_S$.

As regards the small signal AC fluctuation of the site-binding charge, ENBIOS implements the following first order model equations:

$$\frac{dn_{SiOH}}{dt} = -k_A^f n_{SiOH} + k_A^b n_{SiO} n_{H^+}^S$$

$$\frac{dn_{SiOH_2^+}}{dt} = -k_B^f n_{SiOH_2^+} + k_B^b n_{SiOH} n_{H^+}^S$$

where k_A^f, k_B^f (in s^{-1}), k_A^b, k_B^b (in m^{3}s^{-1}) are the forward and backward reaction constants, and are related to the equilibrium constants by the relations $K_A = \alpha \cdot k_A^f / k_A^b$, $K_B = \alpha \cdot k_B^f / k_B^b$ where $\alpha = 1/(1000 \cdot N_A)$, N_A being Avogadro's number. The n_i terms denote the volume densities in m^{-3} of the chemical species i. Due to lack of suitable calibration data, at the moment these constants are given default values only for SiO$_2$ and the AC site-binding charge cannot be included in simulations other than for the SiO$_2$ and "custom" insulators. Note that at the time of writing the temperature dependence of the reaction constants is not modeled in ENBIOS.

Compact layer

As of version 3.0 the thin compact layer of specifically absorbed ions at the insulator/electrolyte interface (so-called Stern layer) can be modelled in ENBIOS-1D Lab as a separate thin dielectric layer by switching on the compact layer option in the "Insulator(s)" folder. Compact layer parameters are the relative permittivity, the thickness and the surface charge density at the compact layer/electrolyte interface (in units of elementary charges per square meter). Note that if both the DC site-binding charge and the compact layer are active, then the site-binding charge will be placed at the insulator/compact layer interface while the compact layer surface charge will be placed at the compact layer/electrolyte interface, thus modeling accurately the site-binding charge at the insulator surface and the charge of the adsorbed layer of ions, respectively.

Discretization and meshing

At the start of the simulation, ENBIOS-1D Lab creates the **discretization grid** and stores it in the user memory area for later use. The grid spacing scales according to the Debye length in the region. The meshing algorithm is partly empirical and can give rise to sub-optimal point allocation under some circumstances. ENBIOS-1D Lab does not allow the user to change the mesh generation criteria. The grid is kept constant unless the insulator thickness or other geometrical or physical parameter is changed, in which case ENBIOS generates a new grid upon start of the simulation. It is advisable to clean the disk space of these files periodically.

Solution

The input parameters are sometimes constrained within predefined ranges. The chosen default limits should ensure convergence within acceptable accuracy in most cases of practical interest. However, given the large number of parameters that the user can change, it may happen that convergence is not reached for some combinations of them. In order to cope with these difficulties a convergence criterion parameter is available to expert users in the "Environment" folder. The parameter represents the maximum L^2 norm of the charge error, and by default it is set to 10^{-25} C, that is, approximately 10^{-6} electron charges (q=$1.602 \cdot 10^{-19}$ C), a rather stringent limit that should ensure accurate results even at the highest salt concentrations and in the most demanding conditions. Values up to one electron charge should be sufficient to reach adequately accurate results in most operating conditions.

If high ion concentrations are reached locally in the domain, reaching convergence to a physically meaningful solution can become critical. As a rule of thumb, the ion concentration should never exceed the limit set by the criterion

$$n(\vec{r}) \frac{4}{3} \pi a^3 > 1$$

where a is the ion radius. If this inequality is satisfied, then calculations predict more than one atom in the volume occupied by only one of them, a clearly unphysical situation. Thus, not only the numerical convergence might be affected, but the results will be inaccurate. In fact, the PB equation does not account for steric effects (volume exclusion) at the interfaces. Under these circumstances a modified PB (MPB) equation should be used [Borukhov2000]. However, the MPB equation is not implemented yet in ENBIOS. Typical ionic radii are reported in [Markus1988]. In many cases of practical interest, sufficient accuracy can be retrieved up to moderate bias and salt concentrations by introducing a thin dielectric layer at surfaces in contact with the electrolyte. This layer mimics the thin compact/Stern layer at the Electrolyte/Insulator interface provided its thickness and permittivity take adequate values. Typical parameters for the compact layer are: thickness equal to the counterion radii ($a \approx 0.25$ nm, [Markus1988]), relative pemittivity $\varepsilon_r \approx 5-10$ (typically =7), for a corresponding total capacitance $C_{Stern} \approx 25$ µF/cm^2.

Outputs

ENBIOS-1D Lab supports a list of outputs as illustrated in Figure 4. First come the DC potential, ion concentrations (all anions and cations) and free carrier concentrations (electrons and holes, if a semiconductor region is present) as a function of distance across the structure. By default ENBIOS-1D will plot each quantity only in the relevant region (Electrolyte for the ion concentrations, Semiconductor for the carrier concentration) and with the most common units (mol/dm^3 for ions and cm^{-3} for carriers). The option "all charged particle concentrations" plots both ions and carriers across the whole domain in the same units (m^{-3}, for ease of comparison) and the local total volume charge density. Note that the default oxide thickness (3 nm) is much smaller than the depth of the Electrolyte or Semiconductor regions. Therefore, the Insulator will be hardly visible in a default full zoom-out plot.

Then come the corresponding AC quantities as a function of position and for all frequencies in the sweep. The user is alerted that the Magnitude/Phase plots tend to be more noisy than the Real/Imaginary part ones, especially at high frequency. As of Ver.2.0 ENBIOS plotting routines have been improved to eliminate spurious glitches due to previously active interpolations. As of version 3.0 H$^+$ and OH$^-$ concentrations also appear in the plots. Since the "Result" page is setup by default in autoscale mode, noisy parts of the traces where numerical accuracy has been reached may be visible under some circumstances. The Rappture interface provides many means to easily customize the plot scales to the user needs. Finally, the device Admittance and Impedance can be shown in Real/Imaginary or Magnitude/Phase formats; a Cartesian (Nyquist) plot option is also available (x=Re(Y), Y=Im(Y)).

Bias and frequency sweeps allow the user to visualize all relevant quantities in sequence at each bias point or frequency. If a bias sweep has been set, then AC quantities are accessible only for the last DC bias point in the sweep. The Rappture interface also allows users to hide some of the curves and get less crowded plots than the standard menu would otherwise show.

Appendix A:

The "implicit pH" method is available to study simple situations where the user selects the desired electrolyte ion composition assuming that these ions do not contribute to the pH. In fact, the list of available salts with the "implicit pH" option on (NaCl, KCl, NaNO$_3$ and KNO$_3$) does not contain H$^+$ or OH$^-$. This method, does not prevent users to include the "site-binding charge" and specify the desired pH. In fact ENBIOS adds additional H$^+$ and OH$^-$ ions in proportion to the pH and in equal measure to maintain charge neutrality. The aim of this method is allow a rather complex user-defined electrolyte composition that will not be affected by the selected pH. To obtain this condition, let's recall the site-binding charge equation as a function of the pH (pH=-log$_{10}$([H$^+$])):

$$\sigma_{sb} = qN_S \frac{10^{-2 \cdot pH} - K_a K_b}{10^{-2 \cdot pH} + 10^{-pH} K_b + K_a K_b} \qquad \text{eq. A}$$

or equivalently as a function of the pOH (pOH=-log$_{10}$([OH$^-$])):

$$\sigma_{sb} = qN_S \frac{10^{-2 \cdot (14 - pOH)} - K_a K_b}{10^{-2 \cdot (14 - pOH)} + 10^{-(14 - pOH)} K_b + K_a K_b} \qquad \text{eq. B}$$

These are the site-binding charge equation implemented in ENBIOS-1D Lab. In order to limit the impact of the H^+ and OH^- ions on the user-selected ions composing the electrolyte, ENBIOS-1D Lab uses the following schemes:

- eq. A for pH > 7: $[H^+]=[OH^-]=10^{-pH}$
- eq. B for pH ≤ 7: $[H^+]=[OH^-]=10^{-(14-pH)}=10^{-pOH}$

These expressions enforce that H^+ and OH^- ion concentrations are always ≤ 0.1 µM, thus negligible for a broad range of electrolyte concentrations.

Appendix B:

The "explicit pH" method allows the user to define the acid/base composition of the electrolyte that defines the solution pH.

Let's suppose that we want to simulate a solution of 1 mM NaCl at pH=4. To obtain pH=4 we select 100 µM of a strong acid (e.g. HCl). The reaction equations are:

$$NaCl_{(aq)} \Leftrightarrow Na^+ + Cl^-$$

$$HCl_{(aq)} \Leftrightarrow H^+ + Cl^-$$

$$H_2O \overset{K_w}{\Leftrightarrow} H^+ + OH^-$$
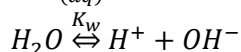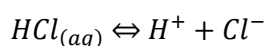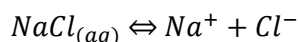
The unknowns are four, $[Na^+]$, $[H^+]$, $[Cl^-]$ and $[OH^-]$, thus we need four equations. i) Na^+ ions are produced only from the dissociation of NaCl (mass balance equation), ii) the Cl^- ions are produced by the dissociation of HCl and NaCl (mass balance equation), iii) the equilibrium constant of water defines the rate between H^+ and OH^- ions, and iv) the charge neutrality equation. These four equations are here reported in a compact way:

i) $\quad [Na^+] = [NaCl]$
ii) $\quad [Cl^-] = [NaCl] + [HCl]$
iii) $\quad K_w = [H^+] + [OH^-]$
iv) $\quad [Na^+] + [H^+] = [Cl^-] + [OH^-]$

By composing these equations we get a second order equation in $[H^+]$ with only one feasible solution:

$$[H^+]^2 - [H^+][HCl] - \frac{K_w}{[H^+]} = 0$$

Once $[H^+]$ is calculated the other unknowns can be obtained straightforwardly.

For more complex chemistry of the electrolyte it is suggested to use on-line pH calculators and the "user-defined" electrolyte option implemented in ENBIOS.

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