Well Posed PNP

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We consider a system in which boundary conditions and equations for electric current are always identically behaved. “Electricity comes first”. We then deal with the fluxes.

The system we describe is a standard electrochemical cell, as used for more than a century, modified to have an insulating partition and lipid bilayer separating two ‘baths’.

The boundary conditions specify the electrical potential and total current (of all types, more about this later). Either we can use voltage clamp (electrical potential specified and total current measured) or we can specify ‘current clamp’ (total current specified and electrical potential observed). We use voltage clamp. The voltage in fact that forms the boundary condition is that observed some distance from the electrodes that pass the electrical current, in the best setups. This ‘four electrode’ arrangement means that the voltage observed is independent of boundary layers near the electrode. If no sign of boundary layers is found experimentally, the potential at the current electrode can be measured.

The fluxes are governed by the Nernst Planck equations, where we use the Einstein relation and diffusion coefficients to avoid confusion between the two definitions of mobility in the literature. When sufficient experimental information is available, the mobility and diffusion coefficient should be treated separately with appropriate physical models for each.

$$I_i = -z_i D_i F \nabla c_i - \frac{z_i^2 D_i c_i F^2}{RT} \nabla \phi \qquad (1)$$

We will first ignore capacitive currents within the baths.

The total current observed includes a capacitive current in addition to the I_i produced by

1) stray capacitance in the setup
2) capacitance to ground from the electrode, wires, and amplifier inputs/outputs connected to the (non zero) electrode. Because one electrode is set to zero, this capacitance to ground is indistinguishable from the stray capacitance (1).

Typical values of the capacitance would be 50 pF although it can be substantially higher (~200 pF) if the set up is sloppily built and substantially smaller (5 pF) if the setup and electronics are particularly well designed

Thus, the total current is **(where the signs need to be carefully checked)**

$$I = \sum_{I=1}^{N} I_i - C\frac{\partial V}{\partial t} = -C\frac{\partial V}{\partial t} - \sum_{I=1}^{N} z_i D_i F \nabla c_i - \frac{z_i^2 D_i c_i F^2}{RT} \nabla \phi \qquad (2)$$

Issues of well posedness arise if the capacity current is neglected. If the capacity current is neglected, all sorts of strange build up of charge can occur at short times, particularly if ionic currents are small or negligible. The **capacitance is always present, without exception,** and so it must be included in the equations to avoid unrealistic description and behavior.

A different problem arises (typically at long times) because one cannot specify the fluxes of *N* types of ions, $i = 1, 2, 3, \ldots N$ and also current. In the real world, current always is specified, because the electrical forces and terms dominate. So we must find a way to deal with the one extra ionic current which we will call I_m.

We do this in two steps:

1) In all setups there is a significant 'leak conductance' of uncertain origin that carries a steady current across the system. This lead conductance allows current at $t \to \infty$ and so it prevents the unlimited build up of concentration.
2) In most experiments, one ion is clearly of less interest and so one can create a leak pathway specific for that uninteresting ion in the model and equations and describe it by a diffusion coefficient. The current through the pathway is just that computed for a single Nernst-Planck species by equation (1) for species *m* if one wishes. OR one can use any other representation that allows a self consistent treatment of the leak current.
3) One must check in the calculations that the assumptions about the leak have no effect on the results of the calculations (in the domains of interest) or that the assumptions describe the leak that is actually present in the experiments.

Finally, we turn to the capacitance from the baths to ground.

Here, the classical approach uses the continuity equation with net charge ρ.

$$\rho = \sum_{i}^{N} z_i e c_i \tag{3}$$

$$\nabla \cdot J_i = -\frac{\partial \rho}{\partial t} \tag{4}$$

or equivalently

$$\nabla \cdot I_i = -z_i F \frac{\partial \rho}{\partial t} \tag{5}$$

for *n* independent fluxes. And the total current equation is more or less ignored.

Here is the new stuff

But we are going to have $N\text{-}1$ ionic current equation**s AND one different kind of equation,** involving the **TOTAL CURRENT** I, not the individual ionic currents I_i. This new equation will include a capacitive current produced by the time rate of change of the net charge $\rho = Q = \sum_{i=1}^{N} z_i F c_i$.

$$\nabla \cdot I = \nabla \cdot \left(\sum_{i=1}^{N} I_i \right) = -\frac{\partial}{\partial t} \sum_{i=1}^{N} z_i F c_i \tag{6}$$

I suggest adding an additional fact, namely the approximation that there is a self-energy, a capacitance to ground between the net charge ρ and the nearby grounded plate always present in experiments.

We then use the definition of capacitance $Q = \rho = C_{\text{capacitance}} V$ and get the **new equation**. Here the capacitance $C_{\text{capacitance}}$ acts as a new constraint on the system.

$$\nabla \cdot I = -\frac{\partial}{\partial t} \sum_{i=1}^{N} z_i F c_i = -C_{\text{capacitance}} \frac{\partial \phi}{\partial t} \tag{7}$$

$C_{\text{capacitance}}$ is both a real parameter (say 150 pF for a 30 cm^2 bath, giving 5 pF/cm^2 specific surface capacitance) and an adjustable damping parameter. As long as the slowest charging time is < 2µsec, this is fine for biological work.

Miscellaneous Equations

$$
\begin{aligned}
I_i &= -z_i D_i F \nabla c_i - z_i^2 u_i c_i F^2 \nabla \phi \\
u_i &= \frac{D_i}{RT} \\
I_i &= -z_i D_i F \nabla c_i - \frac{z_i^2 D_i c_i F^2}{RT} \nabla \phi
\end{aligned}
\tag{8}
$$