ORIGINAL PAPER

The inner potential in electrochemistry

Elizabeth Santos[1] · **Wolfgang Schmickler**[1]

Abstract

Although the inner potential plays a fundamental role in electrochemistry, its precise definition is not clear. In fact, there are two different concepts: a physical quantity which can be measured by high energy electron scattering and calculated by density functional theory. For water, it is of the order of 4 V, and it is irrelevant for electrochemistry. For our purpose, the relevant quantity is the electrostatic potential experienced by an ion, which enters into the electrochemical potential. This is of the order of 0 to −0.5 V, and may be slightly different for different ions.

Keywords Inner potential · Electrochemical potential · Density functional theory · Electron scattering

Electrochemical reactions involve charge transfer between different phases, which are governed by differences in the electrostatic potential. Therefore, the various concepts of potential that exist in electrochemistry are of central importance, and must be clearly defined and understood. Unfortunately, the concepts are not as clear as one wishes, or as textbooks want to make us believe. The textbooks start from a macroscopic picture of an electrochemical system, where the various types of potential are clearly defined — for a recent discussion of this topic, see the article by Fletcher [1]. But if one looks at the structure of an electrolyte solution at an atomic level, concepts like the inner or the surface potential lose their exact meaning.

It is common to start with the definition of the outer potential. To quote from our own book [2]: The *outer* or *Volta potential* ψ_α of a conducting phase α is the work required to bring a unit point charge from infinity to a point just outside the surface of the phase. By "just outside," we mean a position very close to the surface, but so far away that the image interaction with the phase can be ignored; in practice, that means a distance of about 10^{-5} to 10^{-3} cm from the surface.

The outer potential can be measured, e.g., by a technique called the vibrating condenser, whose details need not concern us here. In fact, measuring the outer potential during an electrochemical experiment is cumbersome, and hardly ever done. What one usually measures are differences in the inner potential, which we proceed to define:

The *inner* or *Galvani potential* ϕ_α is defined as the work required to bring a unit point charge from infinity to a point *inside* the phase α; so this is the electrostatic potential which is actually experienced by a charged particle inside the phase.

In our textbooks, we hasten to add: Unfortunately, the inner potential cannot be measured: If one brings a real charged particle — as opposed to a point charge — into the phase, additional work is required due to the chemical interaction of this particle with other particles in the phase. For example, if one brings an electron into a metal, one has to do not only electrostatic work, but also work against the exchange and correlation energies.

The difference between the inner and the outer potential defines the surface potential — see Fig. 1: $\chi = \phi - \psi$. It is caused by an inhomogeneous charge distribution at the surface.

The problem with the inner potential is not only that it is impossible to take a test charge into a phase, the question is also: Where should we place it? Fig. 2 shows a snapshot of an electrolyte solution. Obviously the potential near an oxygen end of water will be much more negative than next to a hydrogen, and this difference is even greater if we consider positions next to an anion and a cation.

Strangely, none of the textbooks we consulted, including our own, mentions this principal difficulty. So is the inner potential the spatial average of the electrostatic potential? And if yes, what happens at the positions of the atomic nuclei, where the potential diverges?

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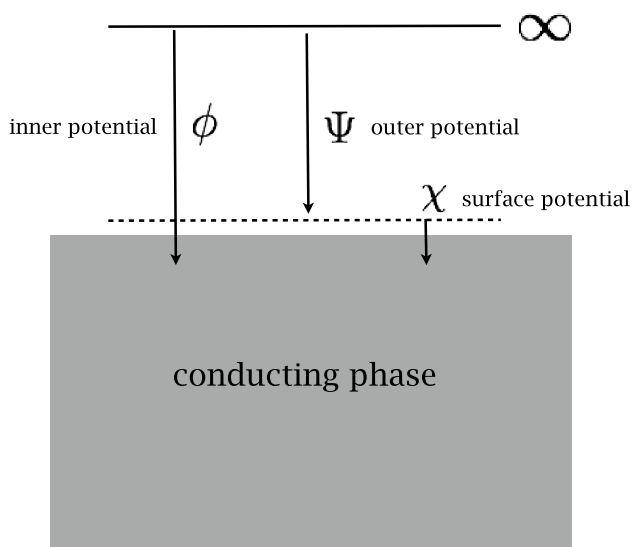
Fig. 1 Inner, outer, and surface potential of a conductor

Before we discuss this question, let us see what the inner potential is actually used for. It occurs in the electrochemical potential of an ion, which is the energy required to take an ion from inside the solution to a position just outside:

$$\tilde{\mu} = \left(\frac{\partial G}{\partial N} \right)_{p,T} \tag{1}$$

where G is the Gibbs energy of the phase under consideration, p and T denote the pressure and temperature, and N the number of particles of the ion. When a phase is in equilibrium, $\tilde{\mu}$ is constant, so it does not matter from which position the ion is taken. It is a measurable quantity, and for an uncharged phase it is the same as the real free energy of solvation, if the reference point is chosen immediately above the solution.
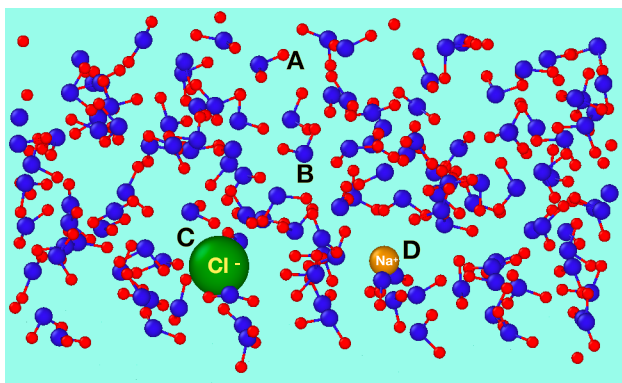
Fig. 2 Snapshot of an aqueous electrolyte. The electrostatic potential at position A next to an oxygen atom (red) or at C next to an anion will be much more negative than at B next to a hydrogen atom (white) or D next to a cation

Obviously $\tilde{\mu}$ measures the interaction of the particle with its environment. It is common to split this into a chemical and an electrostatic part:

$$\tilde{\mu} = \mu + ze_0\phi \tag{2}$$

where μ is called the chemical potential, which contains the short-ranged chemical interaction with the particle's neighbors. The second term is the interaction with the long-range electrostatic part; z is the charge number of the ion, and e_0 the unit of charge.

The two parts cannot be measured individually, and the division is somewhat arbitrary, since arguably all chemical interactions are ultimately based on electrostatics. Nevertheless, Eq. (2) is the basis for the use of the inner potential in electrochemistry. When we measure a voltage, a potential difference, in electrochemistry, we measure it as the difference in the electrochemical potentials of the electrons in two wires, the leads, which have the same composition. Since the chemical potential μ for the electrons is the same in the two wires, the voltage is the difference in the inner potentials of the electrons. So one of the most important quantities in electrochemistry is measured as the difference of a quantity, about whose definition we are not really sure!

As already briefly mentioned, when a phase is in equilibrium, the electrochemical potentials of its constituent particles are constant. Likewise, if the interface between two phases is in equilibrium with respect to the exchange of a certain particle, the electrochemical potential of that particle is the same in both phases: $\tilde{\mu}_\alpha = \tilde{\mu}_\beta$ where the Greek indices denote the phases. When the chemical potential of the particle is not the same in both phases, there is a difference in the inner potential:

$$ze_0(\phi_\alpha - \phi_\alpha) = ze_0\Delta\phi = \mu_\beta - \mu_\alpha \tag{3}$$

Again, the difference $\Delta\phi$ cannot be measured directly. In a typical case, one phase is an electrode, the other an electrolyte. The electrolyte is then connected to a reference electrode, and a voltmeter is connected to the latter and to the electrode. The measured voltage differs from $\Delta\phi$ by an unknown constant, which depends on the reference electrode. When an external potential is applied to the electrode, a double layer of charges forms at the interface, and $\Delta\phi$ changes by the potential across the double layer. Since the potential of the reference electrode is not affected — that is why it is called a reference electrode — the measured change in the voltage equals the change in $\Delta\phi$.

Since the inner potential is so important, and at the same time elusive, many attempts have been made to estimate or calculate it. Limiting ourselves to water, the central question is: What is the inner potential of pure water? If the reference point is chosen just above the surface, the inner potential equals the surface potential χ. Early estimates assumed that

the hydrogen ends of the water molecules at the surface would tend to form hydrogen bonds with the water below, giving rise to a surface dipole with the positive end pointing towards the bulk. This predicted a small positive value for the surface potential, up to a few tenths of an electronvolt. The situation has been well reviewed by Battisti and Trasatti [3], who provide the references to earlier work.

With increasing computer power, molecular dynamics or Monte Carlo simulations could be performed for classical ensembles. A variety of water models were devised, and, amongst other problems, applied to the calculation of the surface potential, which was determined as the average potential in the bulk of water, when the potential above the surface was set to zero. It turned out that the simple classical picture was oversimplified. Not only the dipole but also the quadrupole moment contributes to the inner potential, and the surface effect is not limited to the top water layer. Most water models give values of the order of $\xi \approx -500$ mV [4], a larger magnitude than expected, and of the opposite sign.

In the classical water models, the charges on the oxygen and hydrogen atoms of the molecule are represented as point charges, and are fixed. Naturally, the sum of all charges vanishes. When taking the average over an ensemble of water molecules, the Coulomb divergences pose no problem, since in spherical coordinates the volume element for integration over the radial distance r is $r^2 \, dr$, which cancels the $1/r$ pole.

A value of this order of magnitude is supported by the calculations of Shi and Beck [5] based on DFT. As mentioned above, the surface potential enters into the real free energy of solvation of ions. These authors took Na^+ as an example, and calculated the chemical part of the hydration energy with DFT and obtained a value of -3.9 eV. This corresponds to the chemical potential. The experimental value for the real free energy of hydration, i.e., the electrochemical potential, is -4.4 eV, from which they deduced an inner or surface potential of -0.5 eV. Both the calculation and the experiments have an error margin of the order of ± 0.2 eV.

This raises questions to which we will return later: Is the inner potential the same for all ions? Do they all experience the average electrostatic potential of the phase, or does the calculated value only hold for Na^+?

Before we discuss this, we introduce an entirely different concept of the inner potential. The average electrostatic potential of water generated by all the molecules can be determined by the scattering of high energy electrons. Experimental values are highly positive, about 3.5 to 4.5 eV [4, 6]. They are supported by DFT [7, 8] calculations, which give results of the same order of magnitude, though the values obtained depend somewhat on the basis set, the functional, and the pseudopotentials employed.

Such high positive values are supported by sound physical arguments [9–11]: They are caused by the very uneven spatial distribution of the positive and the negative charge in molecules. The former is concentrated in delta-function like singularities in the nuclei, the latter is spread over the atoms. The argument has been nicely put forward by Bethe [12], who derived the following formula for the average electrostatic potential in a spherical atom:

$$\overline{V} = \frac{2\pi}{3} Z \langle r^2 \rangle \tag{4}$$

where Z is the charge number of the nucleus, and r the radial distance. It is easy to see that the average potential of an atom must be positive, since any sphere surrounding the atom and centered at the nucleus has a positive excess charge, because a part of the compensating negative electronic charge lies outside the sphere.

Obviously, the high positive values for the inner potential cannot be relevant for electrochemistry. They would make the real free energies of hydration for anions by about 7 eV more favorable than those for cations, which is contrary to experiment. The ions experience an average electrostatic potential in vacancies between the water molecules, remote from the atomic nuclei. Therefore, the high positive potential generated by the nuclei has little effect on their electrochemical potential. Recently Becker et al. have estimated the inner potential of water using noble gas atoms as probes. Depending on the kind of atoms, they obtained values in the range of -200 to 100 mV.

We conclude that there are two different concepts of the inner potential: On the one hand, we have the physical value, which is the true average of the electrostatic potential. This is the value measured by high energy electron scattering, and obtained by high-quality DFT calculations. This value is irrelevant for electrochemistry. This implies that DFT calculations for the distribution of the electrostatic potential at electrochemical interfaces must be interpreted with care.

On the other hand, we have the electrostatic potential experienced by the ions. Negative values of a few hundred millivolt as obtained by classical force fields seem reasonable, and are supported by the calculation of the chemical part of the hydration energy reported above. In the classical force fields, both positive and negative ions are represented as point charges, so the positive charges of the nuclei do not dominate the potential. However, the classical force fields have been constructed to reproduce the structure and the energetics of aqueous solutions, so it is not clear how well they represent the electrostatics. In this respect, DFT-based tight binding may offer a good compromise: Its energetics are based on DFT, while the charges are represented as point charges localized on the orbitals, and are obtained from self-consistent calculation. The excess charges are not fixed, but depend on the environment. Thus, local charge fluctuations are accounted for. Our own group has obtained a value of -0.32 V for the inner potential of water, which is not far from the value obtained from force fields or from the works of Shi and Beck [5] or Becker et al. [13].

A question we have not discussed yet in detail is: Do all ions in a phase experience the same inner potential? Textbooks implicitly assume that this must be so, but there is no reason why a small ion like Li^+ should not feel a slightly different inner potential than a big ion like Cs^+, as the simulations by Becker et al. [13] suggest. However, it is important that all ions experience the same changes $\Delta\phi$ in the inner potential. Fortunately this is no problem: Changes $\Delta\phi$ are caused by excess charges, which in conducting phases are accumulated at the boundary, and therefore affect all particles in the interior in the same way.

In conclusion: There are two different concepts of the inner potential. One is the average of the electrostatic potential over all space. This value can be measured by high energy electron scattering, and calculated by DFT. It is of the order of 3.5 to 4.5 V, and is irrelevant for electrochemistry. The electrochemical concept of the inner potential gives the electrostatic energy experienced by the ions. It is not clearly defined, and may be slightly different for different ions; state of the art calculations suggest values in the range of -500 to 0.1 mV. Only differences in the inner potentials experienced by a particular type of ion situated in the same material can be measured, since in this case uncertainties in the definition cancel.

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