The difference between 
Faradaic and Nonfaradaic processes 
in Electrochemistry

P.M. Biesheuvel\textsuperscript{1} and J.E. Dykstra\textsuperscript{2}

\textsuperscript{1}Wetsus, European Centre of Excellence for Sustainable Water Technology, The Netherlands
\textsuperscript{2}Department of Environmental Technology, Wageningen University, The Netherlands

Abstract
Both Faradaic and Nonfaradaic processes can take place at an electrode. The difference between the two processes is clearly discussed in several classical sources, but reference to charge transfer across the metal-solution interface as a defining feature of a Faradaic process, leads to ambiguities. We argue that in a Faradaic electrode process both reactant and product species must be part of a bulk phase which is not the electrode. Then, in a Faradaic process, after applying a constant current, and when the bulk phases have constant composition, the electrode charge, voltage and composition will go to constant values, unchanging in time. Thus, a current-voltage curve, or polarization curve, can be constructed based on data from steady-state experiments. This \( i \text{ – } V \) curve characterizes the Faradaic process. For a Nonfaradaic process, however, charge is progressively stored, and the electrode composition changes in time. To characterize a Nonfaradaic process, we inject a discrete amount of electronic charge in an electrode, equilibrate the system, and record the electrode voltage. Repeating this procedure multiple times, a charge-voltage curve can be constructed based on equilibrium data. For the water desalination method called “capacitive deionization” (CDI) the difference between Faradaic and Nonfaradaic processes is of special importance because both processes occur in CDI.

In electrochemistry and electrochemical engineering, there is a neat distinction between Faradaic and Nonfaradaic processes \cite{1,2,3}. This difference is important because the two processes represent two fundamentally different modes of how an electrode behaves, and how to characterize the electrode (process). Experimentally, for a Faradaic process at an electrode a steady state current-voltage (\( i \text{ – } V \)) curve, or polarization curve, can be constructed, and this makes it categorically different from a Nonfaradaic process, which can be described by an (equilibrium) charge-voltage (\( \sigma \text{ – } V \)) curve. Thus, the proper class of an electrode process can (with some restrictions) be established on the basis of an experiment without knowledge of the chemistry of the electrode process.

Nevertheless, to distinguish between a Faradaic and Nonfaradaic process, it can help when chemical information is at hand: if it is known that there is no charge transfer (reaction) at the electrode, then the process must be Nonfaradaic. However, the reverse is not true: it is not the case that having a redox reaction somewhere in or at the electrode implies the process is Faradaic, as will be explained below. In brief, it is only correct that a redox reaction at the electrode implies we have a Faradaic process when both reactants and products of the redox reaction come from, or go to, a bulk phase that is in contact with the electrode. In this way, electronic charge injected into an electrode, is truly transferred out of it, and is not being stored, see Fig. 1.
The bulk phases around the electrode serve as reservoirs. These are reservoirs in which we automatically have, or can establish, a constant chemical potential (activity) of the ionic, atomic or molecular species involved in the redox reaction, for instance by constantly refreshing the reservoir, or by making it large. For at least one component this bulk phase will be electrolyte (either liquid or solid), in which ions or uncharged molecules are dissolved (or are a constituent of the solvent), but the reservoir can also be a bulk metal phase, as is the case for a plating reaction. Alternatively, the bulk phase can be an oxidic phase, either deposited as a layer on the electrode, or as a solid phase nearby the electrode, as for the products of a corrosion reaction. Ions can also form a solid salt, such as in the lead acid battery, or the AgCl-phase in an Ag/AgCl electrode. Finally, one of the bulk phases can also be the gas phase, e.g., for hydrogen fuel cells.

With reactants coming from such a bulk phase, and products eventually going there, we really transfer charge out of the electrode, and thus have a Faradaic process. In this case we can characterize the electrode process by construction of a polarization curve (i – V curve). This also works when – as is generally the case – products and reactants not only undergo a charge-transfer reaction, but prior to and after that reaction are involved in chemical steps without charge transfer, such as when they adsorb or desorb to/from the surface, associate, dissociate or otherwise react. The key requirement for a process to be Faradaic remains that electronic charge is transferred away from the electrode, which requires the involvement of atoms, ions or molecules as reactants and products, both of which come from, or go to, a reservoir phase. For such a Faradaic process, as long as the external bulk phases do not change their composition (and do not disappear altogether), steady-state operation can be arrived at, where each value of the current corresponds to one value of the electrode potential. In this case, the electrode merely serves as a “meeting place” between on the one hand electronic charge, and on the other hand molecular, atomic or ionic species from a bulk phase. After joining together, they (as the product of the redox reaction) leave the electrode, and they do not stay there.

In contrast, in a Nonfaradaic reactions, electronic and ionic charge does stay in or at the electrode. This is the case when there is no redox reaction at all, or the redox reaction at the electrode involves some atoms that are part of the electrode structure itself, or when the reacting species is oxidized/reduced at the electrode, but then stays there. In these cases there is no true charge transfer across the electrode interface. Then we have a Nonfaradaic, or capacitive, process, for which a σ – V curve can be constructed, and not an i – V curve. Examples are electrodes consisting of an intercalation material such as Prussian Blue Analogue, where the Fe$^{2+}$/Fe$^{3+}$ lattice atoms can be oxidized and reduced [4]; or redox-active ferrocene group immobilized on a carbon surface [5]; or when Li$^+$-ions inside a graphite electrode are reduced to metallic Li which then stays in the electrode.

Next, we provide verbatim texts from three classical book sources that discussed these two kinds of processes in detail. These books are: D.M. Mohilner (1966), T. Erdey-Grúz (1972), and A.J. Bard and L.R. Faulkner (1980), refs. [1–3]. We also provide their words on nonpolarizable and ideally polarizable electrodes, as these terms line up exactly with the difference between a Faradaic and Nonfaradaic process.
Figure 1: Charge transfer vs. charge storage as the key difference between Faradaic and Nonfaradaic processes, using six examples.
Figure 2: Operational differences between Faradaic and Nonfaradaic processes.
Ideal Polarized Electrodes. Ideal polarized electrodes [...] are defined as electrodes at which no charge transfer across the metal-solution interface can occur, regardless of the potential imposed on the electrode from an outside source of voltage.

In a given solution at any fixed potential within the permissible range, the double layer at an ideal polarized electrode attains a true state of equilibrium which can be described precisely in terms of classical equilibrium thermodynamics. However, this equilibrium is not of the familiar nernstian type. Rather, it is a state of electrostatic equilibrium in the electrical double layer. Therefore, to define the state of an ideal polarized electrode at equilibrium, it is necessary to specify not only the temperature, pressure, and composition (chemical potentials) of each phase, but also the value of an additional electrical variable. This electrical variable expresses the degree of charge separation across the interface. Depending on convenience, one may choose for the electrical variable either the excess charge density on the metal $q^M$ or the potential $E$ of the ideal polarized electrode with respect to a reference electrode. Thus, an ideal polarized electrode at equilibrium is a system having one more degree of freedom than it would have were it in a state of nernstian equilibrium. This means that an ideal polarized electrode has the unique capability of being in thermodynamic equilibrium at any potential whatever (within a certain range), although the temperature, pressure, and composition of its phases remain fixed.

Charge-Transfer Electrodes. Electrodes which are not ideal polarized may be called charge-transfer electrodes. At these electrodes the familiar electrochemical processes of oxidation and reduction take place. In terms of the electrical double layer, a charge-transfer electrode is one at which electrically charged particles, ions or electrons, can be transferred across the metal-solution interface. In electrical terminology, a conduction current can flow across the interface of a charge-transfer electrode, but only a displacement current can flow at the interface of an ideal polarized electrode.

For fixed temperature, pressure, and composition of each phase, there is one, and only one, value of the electrode potential for which a charge-transfer electrode may be at equilibrium. This is the potential specified by Nernst's equation. In contrast, for an ideal polarized electrode to be at equilibrium under the same conditions, any of a continuously infinite set of potentials will suffice.

Faradaic and Nonfaradaic Processes. The familiar electrode processes of oxidation and reduction which take place at charge-transfer electrodes obey Faraday's laws; hence they are called faradaic. At an ideal polarized electrode, faradaic processes are prohibited. Whenever a real electrode behaves as an ideal polarized electrode, it is because, within a certain range of potentials, all the faradaic processes which might conceivably take place there fall into either of two categories; (a) The activation energy is so high that the faradaic process occurs at a negligible rate. [...] (b) Even though the activation energy is low, the equilibrium constant for the faradaic process is such that the concentration of either reactants or products is so low as to be meaningless (except in a statistical sense). Therefore, any charge transfer accompanying a change of electrode potential is entirely negligible.

The processes of adsorption and desorption which take place whenever the structure of the electrical double layer changes are not described by Faraday's law; hence they are called nonfaradaic. At ideal polarized electrodes, only nonfaradaic processes can take place, but at charge-transfer electrodes, both faradaic and nonfaradaic processes occur simultaneously.
Polarization and overvoltage. Usually the passage of electric current changes the potential of the electrode, a phenomenon called polarization. Polarization brings about changes in the electrochemical double layer at the electrode surface. As a first approximation, the double layer can be regarded as a capacitor. If ion formation and neutralization are slow, the ions reaching the double layer as a result of current flow tend to increase the charge of the capacitor and the potential between its plates. This fraction of the current, associated with all polarizations, is the so-called capacitive current which stops as soon as the steady state is reached. Since charge transfer always occurs at the electrode, even if it is slow, the double layer can be regarded as a capacitor with some leakage due to a parallel resistance. The fraction of current which is not involved in changing the charge of the double-layer capacitor but passes across the phase boundary by electron transfer has come to be known as faradaic current.

If the faradaic current is disregarded, the amount of charge carried by current \( i \) (A cm\(^{-2}\)) during a time interval \( dt \) into the double layer is given by \( dq = idt \). This causes the potential difference across the double layer to change [...].

Depolarization; Polarizable and non-polarizable electrodes. Upon transferring electric charge to electrodes by means of charge-carrier ions, various changes occur. The charge carriers (ions, electrons) reaching the surface of an indifferent electrode (i.e. one which does not release nor neutralize ions) cannot undergo discharge to form components of neutral particles. Under such conditions, the charge carriers enter the double-layer capacitor located at the phase interface and change the amount of charge on, and the potential difference across, its plates. The change of the potential difference is reflected by the polarization of the electrode. Systems which behave in this manner are ideally polarizable electrodes.

By means of ideally polarizable electrodes, the charge and potential of the electrochemical double layer can be varied freely within certain limits. The variation of these parameters permits the study of the structure of the double-layer.

There is no thermodynamic equilibrium between an ideally polarizable electrode and the solution because there is no common component capable of changing its charge and being transferred between the phases, conditions necessary for equilibrium. The state of an ideally polarizable electrode is well defined only if an external source is used to maintain a constant polarization potential, i.e. the double-layer capacitor charged with a definite charge. The polarization potential is an independent parameter of the system.

Ideal polarizability can only be realized, even approximately, in a limited potential range. In all cases, if the potential becomes sufficiently positive or negative, some electrode processes will start to occur, i.e., charge will be transferred between the plates of the capacitor. If no other process can take place, hydrogen or hydroxide ions will be neutralized from aqueous solutions. As a result, the charge on the plates, and the potential difference between them, will be decreased, i.e. depolarization occurs.

[If] depolarization is strong [...] and the process is fast enough, then metal and solution are in thermodynamic equilibrium. Under such conditions the electrode potential is but slightly changed by current flowing through the electrode. The reason is that changes of charge and potential in the double-layer due to the flow of current accelerate electron transfer. Thus the process becomes fast enough to compensate for any changes of electron concentration on the surface before such changes would cause an appreciable potential shift in the double-layer. The potential of electrodes characterized by large exchange currents is practically unaffected by small current densities (non-polarizable electrodes), and large current densities only affect the potential in so far as the concentration of the potential-determining ions changes around the electrode [...].
Faradaic and Nonfaradaic processes. Two types of processes occur at electrodes. One kind comprises those just discussed, in which charges (e.g., electrons) are transferred across the metal-solution interface. This electron transfer causes oxidation or reduction to occur. Since these reactions are governed by Faraday’s law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called faradaic processes. Electrodes at which faradaic processes occur are sometimes called charge transfer electrodes.

Under some conditions a given electrode-solution interface will show a range of potentials where no charge transfer reactions occur because such reactions are thermodynamically or kinetically unfavorable. However, processes such as adsorption and desorption can occur, and the structure of the electrode-solution interface can change with changing potential or solution composition. These processes are called nonfaradaic processes. Although charge does not cross the interface under these conditions, external currents can flow (at least transiently) when the potential, electrode area, or solution composition changes. Both faradaic and nonfaradaic processes occur when electrode reactions take place.

Nonfaradaic processes and the nature of the electrode-solution interface.

The ideal polarized electrode. An electrode at which no charge transfer across the metal-solution interface can occur regardless of the potential imposed by an outside source of voltage is called an ideal polarized (or ideal polarizable) electrode (IPE). While no real electrode can behave as an IPE over the whole potential range available in a solution, some electrode-solution systems, over certain limited potential ranges, can approach ideal polarizability.

Capacitance and Charge of an Electrode. Since charge cannot cross the IPE interface when the potential across it is changed, the behavior of the electrode-solution interface is analogous to that of a capacitor.

The three books referred to, provide much useful background information about the different electrode processes. However, in some way there remains an ambiguity, because the exact meaning is not made very explicit of what is a charge-transfer process (transfer of charge across the metal-solution interface). The plating out of a Cu$^{2+}$-ion is a Faradaic process, thus is an example of charge transfer across the interface. A very different process is the adsorption of a cation inside a carbon material in which an electrical double layer (EDL) is formed, and this is not associated with charge transfer and is a Nonfaradaic process. Despite the fact that clearly these two examples fall in different classes, if we consider the transport of electrons and ions around the electrode, the two processes are not so different: in both cases, cations move from the electrolyte into an electrode, and at the same time electrons move in as well from the electronic circuit, to compensate for the ionic charge. What is the big difference? Thus what does it mean that charge must be transferred from metal (electrode) to solution (electrolyte) to define a process as Faradaic? For the example of Cu-plating, where is the charge transfer? In plating, cations move to the electrode and become metallic. In terms of charge transfer between solution and metal, this seems not particularly different from the case of cations moving into a carbon (EDL-based) electrode. So, when it comes to the criterion of charge transfer across the metal-solution interface, why is the storage of cations inside the sub-nm pores of a carbon material fundamentally different from the plating out of Cu$^{2+}$-ions? In our view, the answer requires specifying that charge transfer across the metal-solution interface implies that reactants and products both move in and out of the electrode (to adjacent bulk phases), and neither accumulates in the electrode. This requirement is part of the definition of a Faradaic process. This also applies to the Faradaic process of metal plating just discussed, where the reduced Cu-atom is incorporated in the metal bulk phase, while the electrode “grows away”. The electrode is only the very surface of the metal piece.
In distinguishing Faradaic from Nonfaradaic processes, there is a related problem that we encounter if we do not include the specification that reactants and products must move between adjacent bulk phases, for a process to be Faradaic. This is the question, where exactly do we position the interface, to be able to say that a metal-solution charge transfer took place? For an electrode process to qualify as Faradaic, does it suffice when a certain electrode material contains in its structure atoms such as Fe or Mn, which can undergo redox reactions, as for certain intercalation materials? After all, in this case we do have charge transfer from an electron-conducting phase to the crystal lattice [6].

Or another example, when a carbon material is decorated with surface-bound redox-active groups (e.g., based on ferrocene molecules, which can bind an anion), which can be oxidized or reduced, do we here have charge transfer across the metal-solution interface? It is when we define the redox-active groups to be outside the electrode (metal). Instead, if we assign these groups to be part of the electrode, we can still say there is charge transfer across the metal-solution interface if we assign the adsorbing ions from solution to be part of the metal (electrode) as well. So whether we have charge transfer, depends on where exactly we draw the metal-solution boundary. And it may be even more complicated when the adsorbing ion receives a partial charge from the electrode, thereby partially reducing/oxidizing [6]. In that case, there is charge transfer even when we decide that conceptually the ions stay in solution. The necessity for this choice of where to draw the the metal-solution interface shows that the concept of charge transfer is not so straightforward.

We argue that these considerations about where the redox reaction takes place exactly, and where we draw the solution-metal interface to define charge transfer, are not very helpful in distinguishing between a Faradaic and Nonfaradaic process. Instead, another criterion makes the two processes clearly different, one that was also addressed in the sources mentioned above. The defining criterion is whether or not the electrode changes composition upon steady current supply, see Fig. 2. If this is not the case, we have a charge-transfer electrode, i.e., a nonpolarizable electrode, and the process is Faradaic. In a Faradaic process both reactant and product of the redox reaction (via intermediate processes at the electrode), ultimately come from, and end up in, a bulk phase, such as a solid metal, solid salt (layer), electrolyte, or gas phase. In contrast, for an ideally polarizable electrode, and thus a Nonfaradaic process, there is either no redox reaction in or at the electrode at all, or the redox reaction involves an atom, molecule or group bound in or at the electrode. As a consequence, for such a Nonfaradaic process there really is storage of ions and charge, because the overall composition of the electrode changes upon ongoing current supply. In the Faradaic process this is not the case, the electrode does not store charge, and applying a steady current will not change the composition of the electrode over time.

With reference to Fig. 2, let us reiterate the differences between Faradaic and Nonfaradaic processes. First of all, in our view, the difference between the two processes exactly lines up with that between on the one hand non-polarizable electrodes (also called charge-transfer electrodes), and on the other hand (ideally) polarizable electrodes. At several points this is also implied in the three source texts. [Note that for the charge-transfer electrode, upon changing the current, for a brief time, also a capacitive (Nonfaradaic) effect is observed, but after that, this electrode only sustains a Faradaic process.]

Next, we can distinguish the processes based on how they respond to a step change in voltage (panel a and b) or current (panel c and d). Upon a step change in electrode potential (panel a and b), the Faradaic process quickly levels out to a new value of the current (different from before). Instead, in the Nonfaradaic process, after a voltage step change, after some time the current will return back to zero, and it will do so after each step in voltage. The integral of current with time (denoted by * in panel b), is the additionally stored charge). Upon applying a current step (panel c and d), the Faradaic process responds by going to a new electrode potential, while in the Nonfaradaic process, any
ongoing nonzero current will either make the voltage increase without limit, or after a step change
the voltage has a constant plateau before it also starts to increase \[7\]. This second scenario occurs
with an electrode with sufficiently strong interactions between adsorbents, leading (at sufficiently
low currents) to internal phase separation, and a constant electrode potential, until one of the phases
disappears. Two or more voltage plateaus are possible when more than two phases are possible \[8–
10\]. The length of the plateau (** in Fig. 2d) is proportional to the amount of electrode material
tested.

Based on data from such experiments, we can construct two types of defining characteristic curves.
For the Faradaic process, we can construct a current-voltage curve based on steady-state data, the
\( i - V \) curve, or polarization curve, see Fig. 1e. The slope of the curve has the unit of Ohm, and
can be considered a (differential) resistance. For the Nonfaradaic process, the defining curve is very
different, and it is a curve of charge, often defined per amount of electrode material, as function
of electrode potential, see Fig. 1f. The (inverse of the) derivative along the curve is the electrode
capacitance, a property with dimension F or F/g, which is a function of the charging degree.

Let us analyze what happens when the current approaches zero and the system goes to equi-
librium. For the Faradaic process, in this case the electrode potential goes to a value given by the
Nernst equation. This potential depends on the activity of the reactant and product species in the
bulk phases. With the activities (chemical potentials) of these species fixed, there is no way that an
experimenter can modify the equilibrium electrode potential by pushing in charge. The charge would
leak away by the Faradaic reaction, and the system returns to the Nernst potential. Therefore, for
Faradaic processes, the well-known tables for (half-cell) standard electrode potentials apply. All of
this is different in a Nonfaradaic process. Here, an experimenter has control over the equilibrium
electrode potential by injecting extra charge. This is the extra degree of freedom already referred
to by Mohilner \[1\], an extra parameter that must be considered to define the electrode characteris-
tics in a Nonfaradaic process. The existence of this extra parameter, or degree of freedom, is what
distinguishes the Faradaic and from the Nonfaradaic process.

Let us discuss the difference between Faradaic and Nonfaradaic for one specific process, Capaci-
tive Deionization (CDI). CDI is a water desalination technology which uses a set of porous electrodes
that are charged and discharged in a cyclic manner, in this way adsorbing and desorbing ions from
water passing the electrodes \[11\]. During charging, ions are adsorbed in the electrodes, and thus the
composition of the electrode changes both on the metallic side of the metal-solution interface, as well
as on the solution side. As a consequence the electrode potential gradually changes when charging
the cell. In some literature, this process of ion storage has sometimes been described as Faradaic
when redox-active groups in the electrode were involved, also by one author of this document \[12,13\].
However, we argue that this process of ion storage in a CDI electrode is always a Nonfaradaic process,
fitting in with the description of Nonfaradaic processes as described above. Besides ion storage, there
can be true Faradaic processes in CDI, leading to a (small) steady current on top of the capacitive
current. In these charge-transfer reactions neither reactants nor products are stored in the electrode.
An example is the splitting of water in oxygen and protons, or the reverse reaction where oxygen is
reduced to water \[14,15\].
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