Consider a solution containing only inert electrolyte (no faradaic redox couple), in which no charge passes across the electrode-solution interface over a given range of potential. Under these conditions, a change in potential at the working electrode from its equilibrium value necessarily causes a charge imbalance across the interface which must be neutralized by rearrangement of charged species in the solution near the electrode surface. In this sense, the interfacial region can be represented by the two plates of a capacitor, whose capacitance is described by

$$\frac{q}{E} = C$$

where \(q\) is the charge in coulombs stored on the capacitor, \(E\) is the potential across the capacitor in volts, and \(C\) is the capacitance in Farads (F). The situation for one value of applied potential in which the electrode surface is negatively charged is illustrated in Figure 3.

Each time the potential at the electrode is changed, charge will flow (current) at the interface until the capacitance equation above has been satisfied, resulting in what is referred to as a charging current. In actual fact, of course, the situation between the charged electrode and charged species in solution is significantly more complex, with the capacitor model being only a satisfying approximation.

The structure of the so-called double layer actually contains several layers on the solution side, whose thickness and composition greatly affect electron transfer to faradaic solution species. The inner-most or compact layer is composed of solvent, ions, and molecules that are not fully solvated, and which are said to be specifically adsorbed to the electrode surface. The center of this adsorbed layer defines the inner Helmholtz plane, which represents the closest approach of solvated ions to the surface of the electrode. These solvated ions interact with the surface of the electrode in a long-range electrostatic fashion only, and are said to be nonspecifically adsorbed. The center of this second layer defines the outer Helmholtz plane, beyond which these ions are distributed in the diffuse layer, extending into the bulk of the solution only a few hundred Angstoms.² Beyond the diffuse layer, ions are not subject to electrostatic effects initiated by the charged electrode surface. Interested readers will find an extensive discussion of this topic in any good electrochemistry textbook, like that written by Bard and Faulkner.²

Because potential measurement requires two separate electrodes, two distinct interfacial regions exist during the
measurement. The movement of charge across these interfacial regions in the presence of a redox couple is the basis of most commonly employed electrochemical methods.