

Usually, the reaction path consists of a number of reaction steps that precede or follow the actual charge-transfer step, and the rate of each these reaction steps is determined by its kinetic parameters, such as exchange current density, diffusion coefficient or transport numbers. The slowest partial step of this chain is decisive for the rate of the overall reaction. As a consequence, limitations of the reaction rate are often not caused by the electron-transfer step itself, but by preceding or following steps such as the transport rates of the reacting ions to and from the electrode surface.

Transport processes play an important role, because electrochemical conversion can only take place when reaction partners and electrons are available at the same time. Frequently, the reaction substances must be brought to these places or transported away, for example, when the reactions include substances in the dissolved state.

Electrochemical equilibrium is always composed of two reactions, the actual reaction and its reversal. The resulting current/voltage relation is called the “current/voltage curve” or the “current/potential curve”. It is composed of two curves, one for the forward and the other for the reverse reaction. At equilibrium, both reactions are in balance.

The forward and reverse reactions of an arbitrary electrode are shown in Figure 18.1. The horizontal axis represents the electrode potential related to the equilibrium potential E_0 . The vertical axis represents the current density, which is synonymous with the reaction rate.

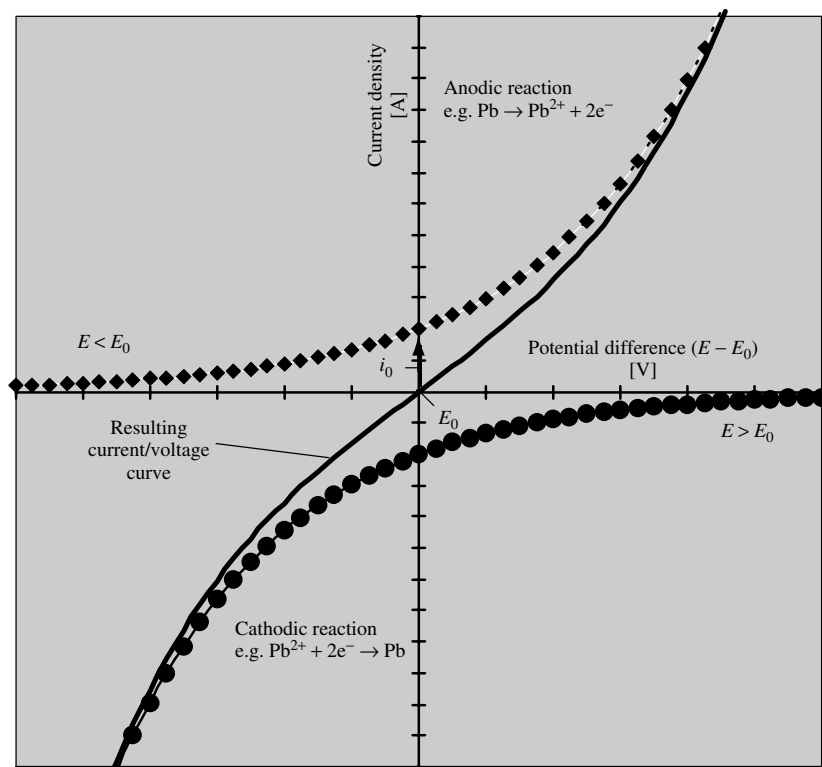


Figure 18.1 Current/voltage curve based on the Butler–Volmer equation (example taken from the lead electrode of a lead-acid battery)