For small overvoltage, the first-order approximation of the exponential terms in the Butler–Volmer equation results in the following equation:

$$(E - E_0)_{\text{trans}} = \frac{R \cdot T}{F} \cdot \frac{i}{i_0}$$

Electrochemical reactions, chemical reactions as well as transport processes that precede or follow the charge/discharge step, lead to changes in the concentration of the reacting substances at the electrode surface and thereby may change the current/voltage curves. Each of these steps can cause an overvoltage. If the diffusion of one of the reacting partners to the electrode surface is the slowest partial step, then the concentration of this substance is reduced more and more with increasing overvoltage. A limit is reached when the concentration of the reaction partner is reduced to zero at the electrode surface. From this point, further increase in overvoltage no longer increases the current. In fact, with rising overvoltage typically a side reaction becomes dominant and the current goes into this reaction. This is the case with the hydrogen evolution at the lead electrode. If the electrode is totally charged and the overvoltage is increasing, the current going into the hydrogen-evolution reaction takes over the complete current through the electrodes. This happens even though the current-exchange density for the hydrogen evolution is several decades smaller than that of the lead charging/discharging reaction.

Diffusion processes can be characterised by a limiting current i_{lim}, which describes the maximum flow of charge carriers that can be transferred through diffusion to the reaction site. The overvoltage of this diffusion process (diff) can be described by the following equation.

$$(E - E_0)_{\text{diff}} = \frac{R \cdot T}{n \cdot F} \cdot \ln\left(1 - \frac{i}{i_{\text{lim}}}\right)$$

An effect not often described explicitly is the "production" of the charge carriers from a chemical process. Typically, this is included in the diffusion overvoltage, but for a deeper understanding of the battery processes and the effects of ageing (diffusion itself is not affected directly by ageing) it is worthwhile to separate these effects.

To explain the effect, the lead acid battery is taken as an example. Figure 18.10 in Subsection 18.4.7.1 will describe the process in more detail. From the electrochemical process described by the Butler–Volmer equation or the Tafel equation charged ions are released into the electrolyte during the discharge process. This increases the concentration c of charged ions in the electrolyte above the equilibrium concentration c_0 (defined by the solubility of the ions in the electrolyte) resulting in a concentration (conc) overvoltage. The following equation gives the mathematical formulation of this overvoltage.

$$(E - E_0)_{\text{conc}} = -\frac{R \cdot T}{n \cdot F} \cdot \ln\left(\frac{c}{c_0}\right)$$

As soon as the concentration of any species in a solution deviates from its equilibrium concentration, chemical processes driven by concentration gradients occur. In the case