The exponential relation between voltage and current is based on the fact that the charge/discharge reaction, in which the electrons are released or absorbed (the so-called "transfer reaction") can be approximately described by an exponential law, called the Butler–Volmer equation.

$$i = i_0 \cdot \left\{ \exp\left[\frac{\alpha \cdot F}{R \cdot T} \cdot (E - E_0) \right] - \exp\left[-\frac{(1-\alpha) \cdot F}{R \cdot T} \cdot (E - E_0) \right] \right\}$$

Therein i is the current density, i_0 the exchange current density, E the actual potential, E_0 the open-circuit electrode potential and α the transfer factor describing the efficiency of the overvoltage on forward and backward reactions. The difference $E - E_0$ is called overvoltage or polarisation. The difference expresses the additional energy voltage required to force the current through the surface. The exponential relation between current and voltage means that the increase in current might be enormous when the overvoltage exceeds certain values.

The equilibrium voltage E_0 is determined by the point at which the forward and reverse reactions are equally fast. In lead acid batteries, this is the point where metal dissolution and deposition balance each other, which means that the current densities of the forward and reverse reaction equal each other. This equilibrium potential represents a dynamic equilibrium: current flow occurs in both directions, but does not appear externally.

The current density for the forward and reverse reactions at the open-circuit potential is called the exchange current density i_0, which describes the rate at which this equilibrium is adjusted. The exchange current density represents an important kinetic parameter. High exchange current density means that the equilibrium potential is rather stable, while a low exchange current density indicates that the electrode potential will be polarised even when very small current densities flow through the electrode. On the other hand, it is important that unwanted side reactions have rather small exchange current densities. In the lead electrode, the exchange current density for the charge/discharge reaction is of the order of 10^{-5} A/cm^2 while it is only of the order of 10^{-13} A/cm^2 for the hydrogen production.[6] Therefore, the hydrogen evolution at open-circuit voltage is rather small.

In the literature, simplified versions of the Butler–Volmer equation can be found. For high overvoltages caused by the electrochemical charge-transfer (trans) process, the so-called Tafel equation is a proper approximation.

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

Using a semi-logarithmic plot results in straight lines, called the Tafel lines. For mathematical reasons, α is signed positive for positive currents and negative for negative currents.

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[6] It is worth noting that the current density caused by the current flow through the electrode during a charge or discharge of a lead-acid battery (approximately 10 h discharge or charge) is of the order 10^{-5} A/cm^2 to 10^{-6} A/cm^2 for the Pb electrode (assumptions: capacity of the lead electrode 3.865 g/Ah, inner surface of Pb active material 0.5 m^2/g and discharge current 0.1 A/Ah). This gives a feeling for the very high activity in equilibrium conditions.