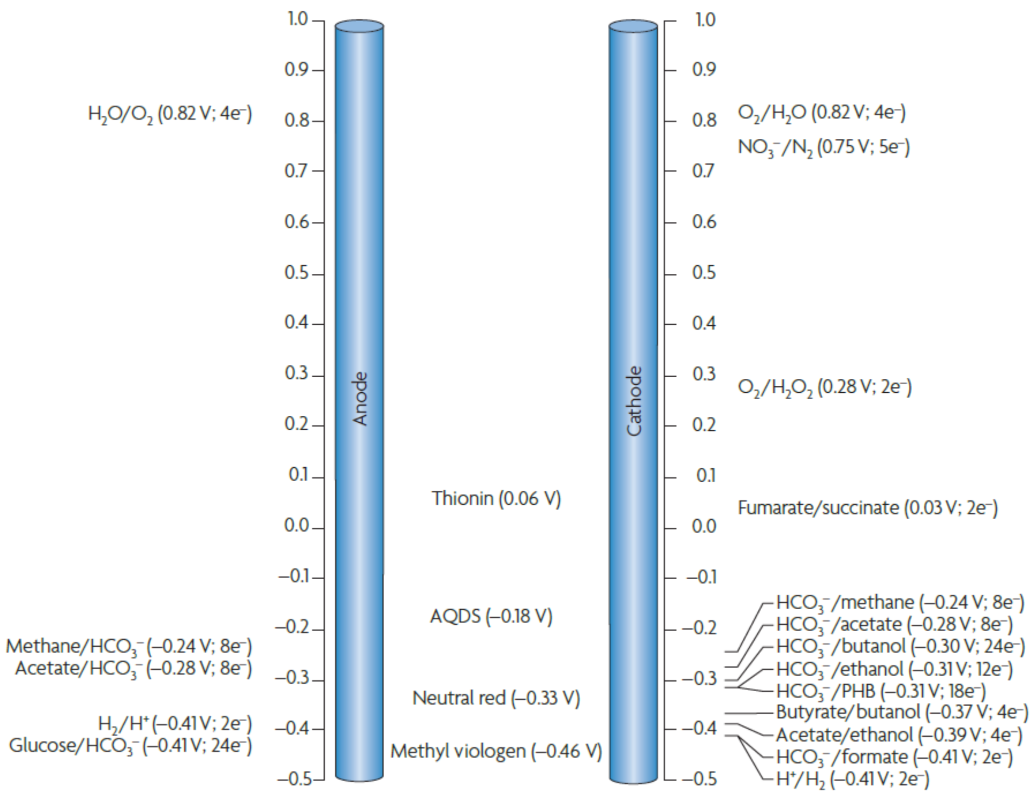
Box 1 | **Theoretical cell voltages**

Bioelectrochemical systems (BESs) can produce power (when they are known as microbial fuel cells) or require an input of power (when they are known as microbial electrolysis cells), depending on the reactions taking place at the electrodes (see the figure*). In a microbial fuel cell, oxidation of an electron donor at the anode (for example, the oxidation of acetate to HCO_3^-; standard electrode potential at pH7 (E'_0) = −0.28 V versus the standard hydrogen electrode (SHE)) is coupled to the reduction of an electron acceptor with a higher electrode potential at the cathode (for example, the reduction of O_2 to water; E'_0 = 0.82 V versus SHE). The resulting cell voltage (cathode potential minus anode potential; 1.10 V in this example) is positive and, thus, power is produced. Conversely, in a microbial electrolysis cell, the oxidation of an electron donor at the anode (for example, acetate/HCO_3^-; E'_0 = −0.28 V versus SHE) is coupled to the reduction of an electron acceptor with a lower electrode potential at the cathode (for example, H^+/H_2; E'_0 = −0.41 V versus SHE). As the resulting cell voltage is negative (−0.13 V), an input of power is required. If water is the electron donor (that is, H_2O/O_2; E'_0 = 0.82 V versus SHE), high energy inputs are required. This illustrates the advantage of bioanodes, which can reduce energy input.

In a BES, microbial reactions that do not proceed through direct electron transfer mechanisms can be catalysed by the use of electron mediators, such as thionin, neutral red and methyl viologen. These compounds can shuttle electrons between electrode surfaces and microorganisms.



PHB, poly-β-hydroxybutyrate. *The electrode potentials of all electron donor and acceptor couples are calculated from Gibbs free energy data, from REFS 99,117, according to the methods described in REF. 13. The E'_0 values of the electron mediators are from REFS 83,118.

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