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Shift between extracellular electron discharge and uptake by electrode-associated *Geobacter metallireducens* biofilms

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The characterization of electrode-mediated microbial reactions has important implications to understanding extracellular electron transfer (EET) reactions potentially occurring in natural settings and also to developing stable bioelectrochemical systems that exploit such EET reactions. One pertinent question is how EET-capable microbes respond to changes in the environment. For example, do EET microbes differentially interact with extracellular substrates, such as minerals or electrodes, under different electrochemical conditions? This study focused on temporal changes between the extracellular discharge of electrons from cells to the environment (anode reduction) and the uptake of electrons from the environment (cathode oxidation) by EET-capable cells colonized on electrodes. Namely, we investigated a metabolic shift in anodically grown *Geobacter metallireducens* biofilms from anode reduction to cathode oxidation in tests with potentiostatically controlled graphite electrodes. *G. metallireducens* biofilms demonstrated a quick and reversible shift between anode reduction and cathode oxidation as a function of electrode potential and availability of nitrate and acetate, which are co-substrates associated with anodic/cathodic reactions. Cathode oxidation was coupled with nitrate reduction by metabolically active biofilms, with a large cathodic current density that was of comparable magnitude to the one recorded in anodic operation of the same biofilm. A quick shift from anode reduction to nitrate-dependent cathode oxidation was thought to be enabled by the presence of nitrate-reducing enzyme activity in the anode-reducing biofilm cells without prior exposure to nitrate. Cyclic voltammetry and the analysis of its first derivative provided insights into electron transfer mechanisms of these biofilms.