

Exogenous electron shuttle-mediated extracellular electron transfer: Electrochemistry and thermodynamics

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Despite the importance of exogenous electron shuttles (ESs) in extracellular electron transfer (EET), a lack of understanding of the key properties of ESs is a concern given their different influences on EET processes. Here, the ES-mediated EET capacity of *Shewanella putrefaciens* 200 (SP200) was evaluated by examining the electricity generated in a microbial fuel cell. The results indicated that all the ESs substantially accelerated the current generation compared to only SP200. The current and polarization parameters were linearly correlated with both the standard redox potential and the electron accepting capacity (EAC) of the ESs. A thermodynamic analysis of the electron transfer from the electron donor to the electrode suggested that the EET from *c*-type cytochromes (*c*-Cyts) to ESs is a crucial step causing the differences in EET capacities among various ESs. Based on the derived equations, both standard redox potential and EAC can quantitatively determine potential losses (ΔE) that reflect the potential loss of the ES-mediated EET. *In situ* spectral kinetic analysis of ES reduction by *c*-Cyts in a living SP200 suspension was first investigated with the E_{ES} , E_{c-Cyt} , and ΔE values being calculated. This study can provide a comprehensive understanding of the role of ESs in EET.

