Metabolic Control Analysis of Bioelectrodes for Multistep Oxidation of Biofuels

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Harnessing the biological process of glucose oxidation for the production of electrical energy represents a challenging but highly important goal in bioelectrochemistry. Biological fuels such as glycerol, glucose and sucrose are abundant and possess high energy density. Complete electrochemical oxidation of these fuels at low temperature requires a multistep enzymatic system coupled intimately with carefully tailored electrodes. Tremendous progress has been made recently in creating electrodes based on the krebs cycle, and demonstrating the impact of "closing the loop" on observed power density. However, the efficiency of electrochemical energy conversion is limited compared to living biological systems. There is a need for quantitative understanding of such systems in order to approach systematic design and optimization.

An example of such a system is shown in Fig. 1, a version of the Krebs cycle wherein pyruvate is oxidized completely to CO_2 by a system of nine enzymes, four of which are NAD(H) dependent enzymes coupled to electrodes. We have developed a kinetic model of this system based on reported experimental results [1], coupled with kinetic parameters for highly active NADH oxidizing electrodes [2]. The model reproduces the observed power density and is suitable for design and optimization purposes.

Metabolic Control Analysis (MCA) was used to characterize the mechanistic steps in the overall pathway. MCA has been applied extensively to understand biological pathways in living organisms, but has seen limited use in other technological fields. The application of MCA to the model pyruvate-oxidizing anode enables the quantification of limitations in the pathway, and optimization of the electrode for maximum energy and power over a range of operating conditions.

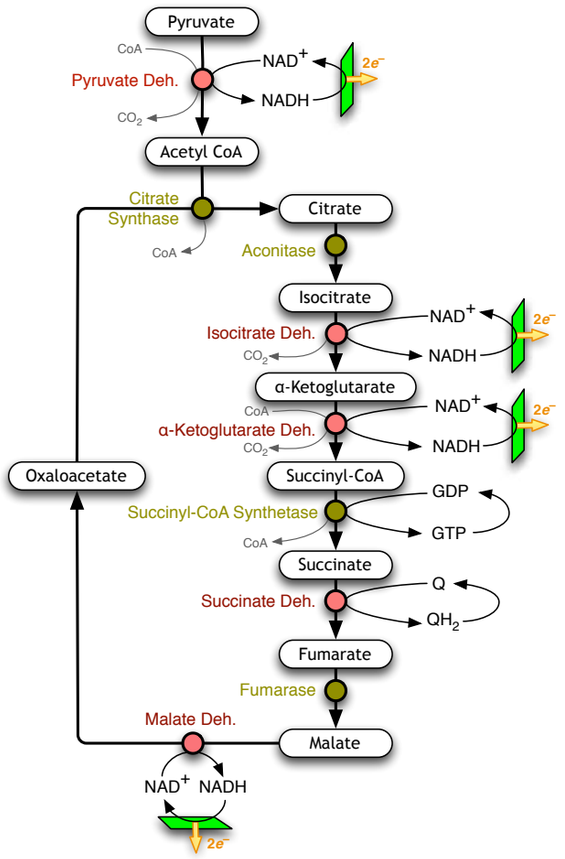

Figure 1. Schematic of Krebs cycle with associated NADH oxidation steps. Redox reaction steps are indicated in red.

REFERENCES

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2. H. Li, H. Wen and S. Calabrese Barton, *Electroanalysis,* **24**, 398-406 (2012).