Available online at www.sciencedirect.com

ScienceDirect

Electrochimica Acta 52 (2007) 2905–2912

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Nanodevices in nature: Electrochemical aspects☆

Alexander G. Volkov[a,*,1], Maya I. Volkova-Gugeshashvili[a],
Courtney L. Brown-McGauley[a], Albert J. Osei[b]

[a] Department of Chemistry and Biochemistry, Oakwood College, 7000 Adventist Blvd., Huntsville, AL 35896, USA
[b] Department of Mathematics and Computer Science, Oakwood College, 7000 Adventist Blvd., Huntsville, AL 35896, USA

Received 16 May 2006; received in revised form 19 July 2006; accepted 29 August 2006
Available online 25 September 2006

Abstract

Electrochemical multielectron reactions in photosynthesis and respiration are evaluated by thermodynamic and kinetic analysis. Kharkats and Volkov [Yu.I. Kharkats, A.G. Volkov, Biochim. Biophys. Acta 891 (1987) 56] were the first to present proof that cytochrome *c* oxidase reduces molecular oxygen by synchronous multielectron mechanism without O_2^- intermediate formation. After this pioneering observation, it became clear that the first step of oxygen reduction is two-electron concerted process. The energy for the H^+-pump of cytochrome oxidase is liberated when the third and fourth electrons are added in the last two steps of water formation independent of the reaction pathway. Electrochemical principles govern many biological properties of organisms, such as the generation of electric fields, and the conduction of fast excitation waves. These properties are supported by the function of a variety of natural nanodevices. Ionic channels, as natural nanodevices, control the plasma membrane potential, and the movement of ions across membranes; thereby, regulating various biological functions. Some voltage-gated ion channels work as plasma membrane nanopotentiostats. In plants, excitation waves are possible mechanisms for intercellular and intracellular communication in response to environmental changes. The role of electrified nanointerface of the plasma membrane in signal transduction is discussed as well.

Keywords: Multielectron reactions; Photosynthesis; Respiration; Proton pump; Phototropism

1. Introduction

Living organisms are intricately designed with systems of "checks and balances" which regulate biological processes, and minimize malfunctions. Biological nanodevices are largely responsible for the nearly flawless function of various organisms. The study of nanodevices has limitless applications in bioelectronics, biology, bioelectrochemistry, genetics, biophysics, bioengineering, biotechnology, and other fields of scientific study.

The electrochemical aspects of various nanodevices in a wide variety of biological processes are discussed. Furthermore, we focus specifically on: nanoreactors in multielectron reactions, the bioelectrochemical function of cytochrome oxidase, electrochemical nanodevices in photosynthesis and phototropism. There are many publications that focus on isolated nanodevices within very specific model systems; however, this approach allows us to analyze the role and significance of nanodevices in a variety of life forms including plants, animals, and bacteria.

Nanodevices are molecules or molecular complexes that have clear and specific functions, and are a few nanometers in size. Millions of nanodevices exist in nature, and we will discuss a few examples. Natural nanodevices include photochemical, electrochemical, and synthetic nanoreactors. Photosystems I and II, enzymes, enzymatic systems in the citric acid cycle, and carbon fixation in the reductive carboxylic acid cycle are also common nanodevices in nature. Molecular motors such as ATP synthase, myosin, kinesin, DNA helicases, DNA topoisomerase, RNA polymerase, and bacterial rotary motors are vital nanodevices that serve to regulate biological processes. Molecules in electron transfer chains act as nanorectifiers and nanoswitches. Biological applications for nanodevices include information transfer, molecular computing, mechanosensors, electroreceptors, magnetoreceptors, magnetosomes, neuronal networks, light sensors, and ion channels.

☆ Presented at the 4th ISE Spring Meeting, 17–20 April 2006, Singapore.

[*] Corresponding author. Tel.: +1 256 726 7113; fax: +1 256 726 7113.
E-mail address: agvolkov@yahoo.com (A.G. Volkov).

[1] ISE member.

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.08.062

2. Multielectron processes in bioelectrochemical nanoreactors

Vectorial charge transfer and molecular recognition at the interface between two dielectric media are important stages in many bioelectrochemical processes such as those mediated by energy transducing membranes [1–5]. Many biochemical redox reactions take place at aqueous medium/membrane interfaces, and some of these reactions are multielectron processes. About 90% of the oxygen consumed on Earth is reduced in a four-electron reaction catalyzed by cytochrome *c* oxidase. Multielectron reactions take place during photosynthesis, which is one of the most important processes on Earth.

Synchronous multielectron reactions may proceed without the formation of intermediate radicals. These radicals are highly reactive, and can readily enter a side reaction of hydroxylation, and destruction of the catalytic complex. Since multielectron reactions do not pollute the environment with toxic intermediates and are ecologically safe, they are used by nature for biochemical energy conversion during respiration and photosynthesis. In the multielectron reaction that takes place in a series of consecutive single-electron stages, the Gibbs energy necessary for a single-electron transfer cannot be completely and uniformly distributed over the stages. The energy demand for various stages is varied, and the excess energy in the simpler stages is converted into heat. In a synchronous multielectron reaction, the energy is used very economically [6–9].

An important parameter in the quantum theory of charge transfer in polar media is the medium reorganization energy, E_s, which determines activation energy. The energy of medium reorganization in systems with complicated charge distribution was calculated by Kharkats [10]. Reagents and products can be represented by a set of *N* spherical centers arbitrarily distributed in a polar medium. The charges of the reaction centers in the initial and final state are z^i and z^f, respectively. Taking R_k to represent coordinates of the centers, and ε_i for dielectric constants of the reagents, it follows that:

$$E_s = 0.8\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_{st}}\right)\left\{\sum_{p=1}^{N}\left[\frac{(\delta z_k)^2}{2a_p} + \sum_{\substack{k=1\\k\neq p}}^{N}\frac{(\delta z_p)(\delta z_k)}{2R_{pk}} + \sum_{\substack{k=1\\k\neq p}}^{N}\sum_{\substack{l=1\\l\neq p}}^{N}\frac{(\delta z_p)(\delta z_l)a_p^3(\vec{R}_{pk}\vec{R}_{pl})}{R_{pk}^3R_{pl}^3}\left(\frac{3\varepsilon_{st}^2}{(2\varepsilon_{st}+\varepsilon_i)^2} - \frac{1}{2}\right)\right]\right\} \qquad (1)$$

where $(\delta z_k) = z_k^f - z_k^i$, $R_{pk} = R_p - R_k$, z_k^f, and z_k^i are charge numbers of particle *k* in the initial and final states, respectively. The term a_p is the radius of particle *p*, R_k the coordinate of *k*-particle center, and ε_i the dielectric constant of reactant. Reactions with synchronous transfer of several charges present a particular case of Eq. (1).

It follows from Eq. (1) that E_s is proportional to the square of the number of transferred charges. Homogeneous multielectron processes are unlikely due to the high activation energy resulting from a distinct rise in the energy of solvent reorganization. For multielectron reactions, the exchange currents of *n*-electron processes are small compared to those of single-electron multistep processes, which make the stage-by-stage reaction mechanism more advantageous. Therefore, multielectron processes can proceed only if the formation of an intermediate is energetically disadvantageous. However, conditions which reduce E_s during transfer of several charges to the level of the reorganization energy of ordinary single-electron reactions can be chosen. These conditions require systems with a low dielectric constant and large reagent radii. Furthermore, the substrate must be included in the coordination sphere of the charge acceptor with several charge donors or acceptors bound into a multicenter complex. Recent papers have presented theoretical studies on the kinetics of heterogeneous multielectron reactions at water/oil interfaces, which proved to be capable of catalyzing multielectron reactions, and sharply reducing the activation energy.

The most effective coupling of ion and electron transport can be obtained if the activation energy of the coupled process is lower than that of the charge transfer in the electron transport chain. It is apparent from Eq. (1) that this requires a simultaneous transfer of opposite charges, so that the second and the third terms of Eq. (1) are negative. An optimal geometry between the centers of charges of donors and acceptors must also be chosen.

3. Cytochrome oxidase: a nanodevice for respiration

The function of the enzymes of the mitochondrial respiratory chain is to transform the energy of redox reactions into an electrochemical proton gradient across the hydrophobic barrier of a coupling membrane.

Cytochrome oxidase (EC 1.9.3.1, PDB 2OCC) is the terminal electron acceptor of the mitochondrial respiratory chain. Its main function is to catalyze the reaction of oxygen reduction to water using electrons from ferrocytochrome *c*:

$$4H^+ + O_2 + 4e^- \underset{\text{photosynthesis}}{\overset{\text{respiration}}{\rightleftarrows}} 2H_2O \qquad (2)$$

Reaction (2) is exothermic, and this energy can be used to transport protons across the mitochondrial membrane (Fig. 1). The enzyme contains cytochromes a and a_3, one binuclear copper complex Cu_a, one mononuclear copper site Cu_b, and one bound Mg^{2+} per monomer. It has a molecular weight ranging from 180,000–200,000 kDa for the most active form [11–13]. Cytochrome oxidases can transport a maximum of eight protons across the membrane per oxygen molecule reduction [14,15]. Four of the protons bind to the reaction complex during the reduction of oxygen to water, and up to four other protons are transported across the membrane. The resulting proton gradient is used in ATP synthesis.

Kharkats and Volkov were the first to present proof that cytochrome *c* oxidase reduces molecular oxygen by synchronous 2:1:1-electron and 0:2:2 proton pump mechanism without the formation of an O_2^- intermediate [7–9,14,15]. The calculations predicted that the first step in oxygen reduction by