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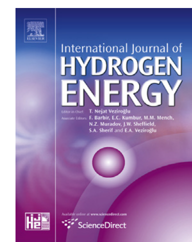

Potassium deficiency, a “smart” cellular switch for sustained high yield hydrogen production by the green alga *Scenedesmus obliquus*

Aikaterini Papazi, Armida-Irene Gjindali, Elizabeth Kastanaki, Konstantinos Assimakopoulos, Konstantinos Stamatakis, Kiriakos Kotzabasis *

Department of Biology, University of Crete, Voutes University Campus, GR-70013 Heraklion, Crete, Greece

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ABSTRACT

Hydrogen is considered to be the future optimal energy carrier, and is expected to contribute to the growth of the world's economy by facilitating a stable supply of energy. The ability of green algae to produce hydrogen was discovered 74 years ago. Since then, several attempts were made, to increase hydrogen production yields, sulfur starvation being the best known. The main concern during these attempts was that the achievable increase in yield was not sustainable. In this contribution, potassium deficiency is presented as a biochemical/bioenergetic switch for a sustained high yield of hydrogen production via the photosynthetic apparatus. Potassium can partially be replaced by sodium in the majority of biochemical processes and as a result the system remains functional. However, sodium cannot replace potassium in the conversion of glucose to starch. This fact significantly increased the yield of hydrogen production through the Photosystem II independent pathway, since electrons originating from the metabolism of glucose are used in the continuous donation to the plastoquinone-pool of the photosynthetic electron chain. Additionally, PSII inactivation (and therefore the inhibition of O_2-production), the further synthesis and over activation of Photosystem I and plastidic hydrogenase, generated a sustained increase in hydrogen production, mainly through the PSII-independent pathway. The self regulation of these multistage processes in hermitically closed static systems of *Scenedesmus obliquus* cultivation, permitted the establishment of anoxic conditions and the continuous electron supply to highly activated hydrogenase, resulting in the sustained high yield hydrogen production and paving the way for future usage in an industrial scale application.
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Introduction

Molecular hydrogen will be the future optimal energy carrier contributing to the growth of the world's economy by facilitating a stable supply of energy [1]. H_2 combustion yields only water thus reducing emissions of carbon dioxide in the atmosphere [2]. At present, most of the world's hydrogen is produced by reforming fossil fuels which is accompanied by the release of carbon into the environment. However,

* *Corresponding author*. Tel.: +30 2810 394059; fax: +30 2810 394408.
E-mail address: kotzab@biology.uoc.gr (K. Kotzabasis).
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hydrogen might be produced from non-fossil renewable resources [2]. In this respect, the light induced conversion of water into hydrogen and oxygen is preferable [2]. One of the perspective ways of obtaining hydrogen from water at the expense of solar energy is to use photosynthetic microorganisms capable of hydrogen production, such as cyanobacteria and green algae [3–7].

It has been known for more than 74 years that unicellular green algae have the ability to produce hydrogen under oxygen depleted conditions. Two mechanisms have been proposed in green algae to account for the origin of reductants involved in the H_2 photoproduction. The first involves the photosynthetic water splitting process of Photosystem II (PSII) and subsequent transport of electrons from water to ferredoxin (Fd) through Photosystem I (PSI) [8,9]. Unfortunately, the hydrogenase in green algae is highly sensitive to O_2, which irreversibly inactivates the enzyme's activity within a few minutes [10]. The second mechanism depends on the metabolic oxidation of stored organic compounds that is coupled to PSI through the plastoquinone (PQ)-pool and results in both H_2 production and CO_2 release [11,12]. Because this pathway also requires light, photosynthetic O_2 evolution is inevitably a byproduct of the reaction and inhibits H_2 production unless it is quickly removed. As a result, H_2 production in microalgal cultures is difficult to be sustained [13].

Except for the above photobiological hydrogen production pathways (PSII-dependent and PSII-independent) there is also another one, known as dark fermentation. Catalanotti et al. [14] recently published a model for hydrogenase activity of *Chlamydomonas reinhardii*, where the dark fermentative metabolism was represented in correlation with the above mentioned photobiological pathways. The majority of microbial hydrogen production through dark fermentation is driven by the anaerobic metabolism of pyruvate, formed during the catabolism of various organic substances [15]. The breakdown of pyruvate is catalyzed by one of two enzyme systems: the pyruvate formate lyase (PFL) or the pyruvate ferredoxin oxidoreductase (PFOR) which transfers electrons to Fd. Reduced ferredoxin transfers electrons to hydrogenase and hydrogen can be produced [15].

Melis and co-workers [16] proved that illuminated *Chlamydomonas reinhardii* cells showed significant H_2 production upon sulfur deprivation. The critical aspect of this observation is the activation of a metabolic switch, which causes an algal culture to change its physiology from aerobic photosynthetic growth to an anaerobic resting rate in the light. The latter is necessary and sufficient to induce H_2 production [17,18]. In sulfur-free medium, the cells down regulate photosynthetic activity particularly at PSII, so that O_2 evolution decreases dramatically [16,19]. At the same time, respiratory activity stays high, so that a sealed algal culture establishes anaerobic conditions and starts to accumulate H_2 after about 1 day [20]. Moreover, the continuity of the process needs to be addressed because hydrogen production by sulfur deprivation of the algae cannot last forever. The yield begins to level off after about 70 h of sulfur deprivation. After about 100 h, the algae need to go back to normal photosynthesis to be rejuvenated by replenishing endogenous substrate [17,21].

An extremely high yield in hydrogen productivity appeared in *Scenedesmus obliquus* cultures when one meta-substituted dichlorophenols (m-dcps) was added to the culture medium [6,7]. Reduced m-dcps, according to their redox potential, take the place of electron donors in the photosynthetic electron flow, close to the PQ-pool. In parallel, the activity of PSII and the release of O_2 were blocked, leading to oxygen-depleted conditions and induction of hydrogenase activity. Additionally, the first step of m-dcps biodegradation (the reduction of m-dcps) supports a continuous circuit between oxidized and reduced m-dcps, which promotes strong electron flow to the PQ-pool, and in turn to Fd and to hydrogenase. Oxygen depletion was achieved not only by the inhibition of PSII activity, but was also induced by the combinational transfer of electrons from reduced m-dcps to the ubiquinone of the mitochondrial respiratory mechanism (cytochromic and alternative pathways) [6,7].

In the present contribution, we tried to face two critical problems that limit the sustainability of hydrogen production in green algae. The first one is the establishment of oxygen depleted conditions without the use of external nitrogen, argon or helium flow, that up to date are required for hydrogenase activation. The second one is to find the switch that will enhance the PSII-dependent and/or PSII-independent pathways, without breaking down the whole microalgal systems, as occurs in sulfur deprived cultures. For these reasons the impact of different element deficiencies on hydrogen production was investigated, and the mechanism of the best of them (potassium deficiency) was revealed. These impacts should be further manipulated in order to fit into an industrial scale use that could supply inexpensive biofuel in an attempt to solve the world's future energy problems.

Materials and methods

Organism and culture conditions

In all experiments axenic cultures of the unicellular green alga *Scenedesmus obliquus*, wild type D3 [22] were distributed into 125 mL hermitically sealed bottles (diameter 5 cm, height 9.5 cm) with an initial concentration of 1 μL packed cell volume (PCV) mL^{-1}. The final culture volume in each bottle was 50 mL of mixotrophic culture medium (addition of 5 g L^{-1} glucose) [23], while the rest was atmospheric air at the beginning of the experiment. The experiments were performed in a temperature-controlled chamber (30 °C) at a light intensity of approximately 100 μE. Sampling took place daily, at the same time, in sterile conditions using sterile needles without opening the bottles. The cultures were manually shaken to achieve complete solubility of the cells in the culture medium before each sampling. The above conditions were the usual ones. Any changes are explained in detail in the appropriate subsection of the results.

GC-TCD measurements of H_2 and O_2

Hydrogen and oxygen measurements were made utilizing gas chromatography, using a thermal conductivity detector (GC-TCD) (Shimadzu GC 2010 Plus, Kyoto, Japan). To separate H_2 and O_2, argon was used as the carrier gas under pressure of five bars and at oven temperature of 120 °C. The column

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