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Review

The cytochrome b_6f complex at the crossroad of photosynthetic electron transport pathways

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ABSTRACT

Regulation of photosynthetic electron transport at the level of the cytochrome b_6f complex provides efficient performance of the chloroplast electron transport chain (ETC). In this review, after brief overview of the structural organization of the chloroplast ETC, the consideration of the problem of electron transport control is focused on the plastoquinone (PQ) turnover and its interaction with the b_6f complex. The data available show that the rates of plastoquinol (PQH_2) formation in PSII and its diffusion to the b_6f complex do not limit the overall rate of electron transfer between photosystem II (PSII) and photosystem I (PSI). Analysis of experimental and theoretical data demonstrates that the rate-limiting step in the intersystem chain of electron transport is determined by PQH_2 oxidation at the Q_o-site of the b_6f complex, which is accompanied by the proton release into the thylakoid lumen. The acidification of the lumen causes deceleration of PQH_2 oxidation, thus impeding the intersystem electron transport. Two other mechanisms of regulation of the intersystem electron transport have been considered: (*i*) "state transitions" associated with the light-induced redistribution of solar energy between PSI and PSII, and (*ii*) redistribution of electron fluxes between alternative pathways (noncyclic electron transport and cyclic electron flow around PSI).

1. Introduction

Photosynthesis is one of the most important processes in nature, which provides the assimilation of carbon dioxide and produces the molecular oxygen using the light energy. In photosynthetic systems of oxygenic type (cyanobacteria, algae, chloroplasts of higher plants), the energy of light quanta absorbed by pigment-protein complexes of photosystem I (PSI) and photosystem II (PSII) is converted into the energy of separated charges, providing electron transfer from the water-oxidizing complex (WOC) of PSII to $NADP^+$ (the terminal electron acceptor of PSI). PSI and PSII are interconnected via the membrane-bound cytochrome b_6f complex and mobile electron carriers, plastoquinone (PQ) and plastocyanin (Pc): $H_2O \rightarrow PSII \rightarrow PQ \rightarrow b_6f \rightarrow Pc \rightarrow PSI \rightarrow NADP^+$. Electron transfer along the chloroplast electron transport chain (ETC) is accompanied by alkalization of stroma (the volume between the chloroplast envelope and thylakoids) and acidification of the internal compartments of thylakoids (lumen), thus generating the transthylakoid difference in electrochemical potentials of hydrogen ions, $\Delta\tilde{\mu}_{H^+}$, which serves as the driving force for operation of the ATP synthase (Mitchell, 1966). The products of the light-induced stages of photosynthesis (ATP and NADPH) are used in reductive biosynthetic reactions of the Bassham–Benson–Calvin (BBC) cycle (Edwards and Walker, 1983).

Elucidation of the regulatory mechanisms, which provide adaptation of photosynthetic organisms to varying environmental conditions, is a topical task of plant physiology and biochemistry (see for review (Cruz et al., 2005; Eberhard et al., 2008; Edwards and Walker, 1983; Foyer et al., 2012; Kramer et al., 2004) and references therein). At the level of ETC, the flexibility of photosynthetic apparatus in response to environmental changes is achieved by cooperation of several mechanisms of the feedback control of electron transport. These mechanisms include the following events: (*i*) optimization of the light quanta partitioning between PSI and PSII, which may be realized upon phosphorylation and relocation of the mobile LHCII

Abbreviations: BBC cycle, Bassham–Benson–Calvin cycle; CEF, cyclic electron flow; ETC, electron transport chain; ISP, iron-sulfur protein; Fd, ferredoxin; FNR, ferredoxin-NADP-oxidoreductase; LEF, linear electron flow; LHCI, light-harvesting complex I; LHCII, light-harvesting complex II; NDH, NAD(P)H dehydrogenase complex; NPQ, non-photochemical quenching; PCET, proton-coupled electron transfer; PSI and PSII, photosystem I and photosystem II, respectively; P_{700}, special chlorophyll pair in PSI; Pc, plastocyanin; PQ and PQH_2, plastoquinone and plastoquinol, respectively; Q, SQ and QH_2, general notations for the three accessible redox states of quinone species – quinone (Q), semiquinone (SQ) and quinol (QH_2); TH, transhydrogenase; $TMQH_2$, trimethylquinol; UQ and UQH_2, ubiquinone and ubiquinol, respectively; WOC, water-oxidizing complex.

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complex ("state transitions") (Allen, 1992, 2003a; Bennett, 1977; Haldrup et al., 2001; Murata, 2009; Lemeille and Rochaix, 2010; Minagawa, 2011; Tikkanen and Aro, 2012, 2014; Tikkanen et al., 2011, 2012; Wollman, 2001); (*ii*) redistribution of electron fluxes through different pathways (noncyclic/cyclic/pseudocyclic electron transport) (Allen, 2003b; Alric, 2010; Asada, 1999; Bendall and Manasse, 1995; Breyton et al., 2006; Johnson, 2011; Joliot and Joliot, 2005; Ivanov et al., 1998; Miyake, 2010; Munekage et al., 2004; Shikanai, 2007); (*iii*) light-induced activation of the BBC cycle enzymes (Andersson, 2008, Buchanan, 1980, 1991; Michelet et al., 2013; Woodrow and Berry, 1988); and (*iv*) pH-dependent regulation of photosynthetic electron transport governed by the lumen and stroma pH (Rumberg and Siggel, 1969; Tikhonov et al., 1981, 1984; Ryzhikov and Tikhonov, 1988; Kramer et al., 1999, 2003; Tikhonov, 2012, 2013). pH-Dependent mechanisms of electron transport control in chloroplasts are associated with the light-induced acidification of the intrathylakoid lumen (pH_{in}) and alkalization of stroma (pH_{out}). Acidification of the lumen ($pH_{in}\downarrow$) causes deceleration of plastoquinol (PQH_2) oxidation by the cytochrome b_6f complex, thus impeding the electron flow between PSII and PSI (Rumberg and Siggel, 1969; Kramer et al., 1999, 2003; Ryzhikov and Tikhonov, 1988; Tikhonov, 2012, 2013; Tikhonov et al., 1981, 1984). Acidification of the lumen also triggers the dissipation of excess energy in the light-harvesting antenna of PSII, thereby protecting the photosynthetic apparatus against a solar stress (Adams et al., 2013; Demmig-Adams, 1990; Demmig-Adams et al., 2012; Li et al., 2009; Müller et al., 2001; Murata et al., 2012; Solovchenko, 2010; Takahashi and Badger, 2011; Tikkanen et al., 2012). The light-induced alkalization of stroma ($pH_{out}\uparrow$ (Heldt et al., 1973; Robinson, 1985)) induces activation of the BBC cycle reactions (Andersson, 2008; Buchanan, 1980, 1991; Woodrow and Berry, 1988), promoting efflux of electrons from PSI to $NADP^+$.

In this review, I will consider the mechanisms of the feedback control of electron transport between PSII and PSI. PQH_2 oxidation at the Q_o-site of the b_6f complex represents the "bottle-neck" link in the ETC between PSII and PSI, which controls the overall rate of the intersystem electron transport. Therefore, the analysis of the problem will be focused mainly on the electron transport events and regulatory processes in the cytochrome b_6f segment of the chloroplast ETC.

2. Brief overview of photosynthetic electron transport chain

PSI and PSII are embedded into lamellar membranes of thylakoids, closed vesicles situated under the chloroplast envelope. Fig. 1 depicts schematically a chloroplast ETC, which provides the electron transfer from PSII to $NADP^+$. Some peculiarities of the structural and functional organization of basic multisubunit protein complexes involved into the intersystem electron transport (PSI, PSII, and b_6f complexes) are briefly considered below.

2.1. Photosystem I

The multisubunit pigment–protein complex of PSI catalyzes the light-induced electron transfer from plastocyanin (or cytochrome c_6 in cyanobacteria) on the lumenal side of the thylakoid membrane to a mobile electron carrier ferredoxin (or flavodoxin) on the stromal side of the membrane (see for review (Brettel, 1997; Fromme et al., 2001; Nelson and Yocum, 2006; Shelaev et al., 2010) and references therein). According to the widely accepted paradigm, a special pair of chlorophyll (Chl) molecules (Chl_{1A} and Chl_{1B}), located at the interface of subunits PsaA and PsaB, forms the primary electron donor named P_{700}. The light-induced excitation of PSI is followed by charge separation between P_{700} and the primary electron acceptor (Chl_{2A} or Chl_{2B}). According to an alternative scheme (Holzwarth et al., 2006; Müller

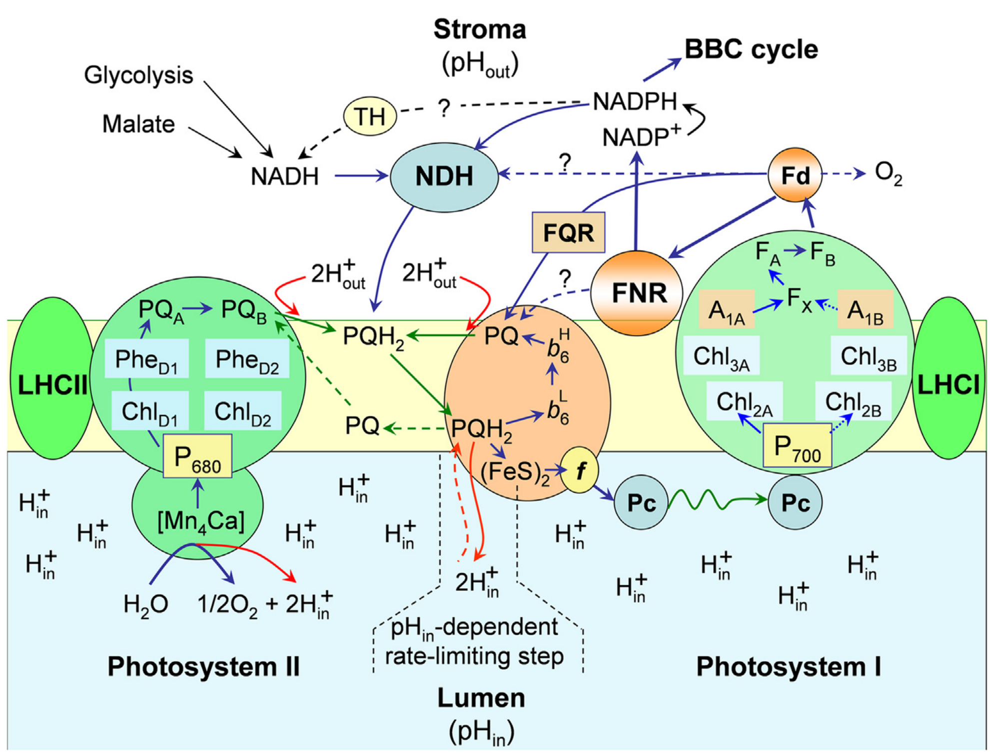

Fig. 1. A scheme of electron transport pathways in chloroplasts and the arrangement of protein complexes (photosystem I, photosystem II, cytochrome b_6f) in the thylakoid membrane. See the list of abbreviations and text for notations and other details.