Investigating the mechanism of thylakoid direct electron transfer for photocurrent generation

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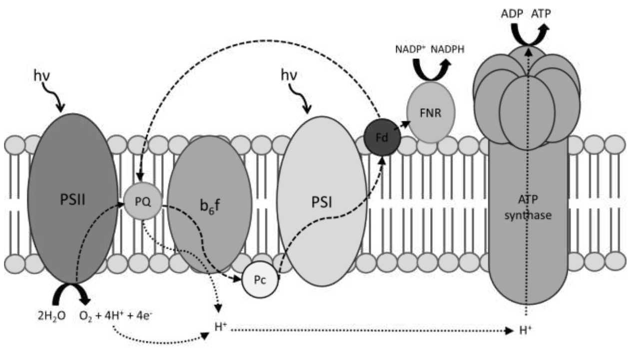

Fig. 1. Schematic of thylakoid membrane showing the components involved in the light-dependent reactions of photosynthesis. Electron flow is shown with dashed arrows while proton flow is shown with dotted arrows.

One of the benefits to using an organelle as a biocatalyst is the possibility for multiple electron transfer pathways at the electrode surface. From Figure 1 it can be seen that thylakoids have a number of electron transfer steps that can be taken advantage of to generate photocurrent in a bio-solar cell. Bioanodes incorporating thylakoids from spinach were studied to determine the mechanism of direct electron transfer to carbon electrodes. These electrodes generated a photocurrent of 0.43 ± 0.02 µA/cm^2. The change in this photocurrent was measured when individual components of thylakoids were removed, inhibited, or activated in order to determine which components contributed to the photocurrent. A decrease in the photocurrent indicates that the component of interest is involved in the DET pathway while an increase suggests the particular component is not involved. The results, as summarized in Table 1, show that photosystems I and II, plastoquinone, cytochrome b6f, and plastocyanin are involved in the direct electron transfer mechanism while ferredoxin and ferredoxin-NADP$^+$ reductase are not.

Table 1. The percent of intact thylakoid photocurrent was calculated for each type of depleted or inhibited thylakoid electrodes: PSII inhibition, PQ removal, b$_6$f inhibition, PSI inhibition, Fd removal, and FNR removal.

	PSII	**PQ**	**b$_6$f**	**PSI**	**Fd**	**FNR**
Percent of intact thylakoid photocurrent	36 ± 7	8 ± 2	61 ± 5	11 ± 2	142 ± 26	146 ± 40

Additional experiments were performed to study the contribution (if any) that ATP synthase has to the photocurrent. Inhibition of ATP synthase at the thylakoid electrodes also leads to a decrease in activity as shown in Table 2, but uncoupling does not restore activity which indicates that the membranes are lysed. Finally, the contribution of the two electron transport pathways in the thylakoid membrane to the photocurrent was determined. Preferential activation of the two electron transport pathways of photosynthesis, by addition of NADP$^+$ for noncyclic and ADP for cyclic, showed that both cyclic and noncyclic pathways contribute to the photocurrent as well. The reported thylakoid electrodes show a contribution of electrons from the first five electron transfer steps in photosynthesis with only the last two steps not participating.

Table 2. The percent of intact thylakoid photocurrent was calculated for each type of thylakoid electrodes: ATP synthase inhibition (ATP), ATP synthase uncoupling (DNP), noncyclic electron transfer activation (NADP), and cyclic electron transfer activation (ADP).

	ATP	**DNP**	**NADP**	**ADP**
Percent of intact thylakoid photocurrent	16 ± 6	25 ± 7	36 ± 5	27 ± 2