Supplementary Information

Increased CODH activity in a bioelectrochemical system improves CO electrosynthesis

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Biological CO/CO_2 conversion via metabolic pathway

The biological CO/CO_2 fermentation used the reductive Acetyl-CoA pathway, so-called Wood-Ljungdahl Pathway (WLP). The WLP is a well-known metabolic pathway of CO_2 fixation. On the other hand, the biological CO conversion to acetyl-CoA consists of two-step processes: water gas shift reaction (WGSR) via carbon monoxide dehydrogenase (CODH) (Eq. 1) and further CO_2 uptake via WLP (Eq. 2)[1].

$$4CO + 4H_2O \rightarrow 4CO_2 + 8H^+ + 8e^- \quad (1)$$

$$4CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2H_2O + 2CO_2 \quad (2)$$

The conventional CO fermentation captures only two moles of carbon from WGSR, and the remaining two moles of carbon are not metabolized due to limited reducing power (Eq. 2). The supplement of additional reducing equivalent by the electrode-based conversion in BES, is able to convert all carbon from CO oxidation, and hence produce additional acetate (Eq 3).

$$2CO_2 + (8H^+ + 8e^-\text{, supplied from BES}) \rightarrow CH_3COOH + 2H_2O \quad (3)$$

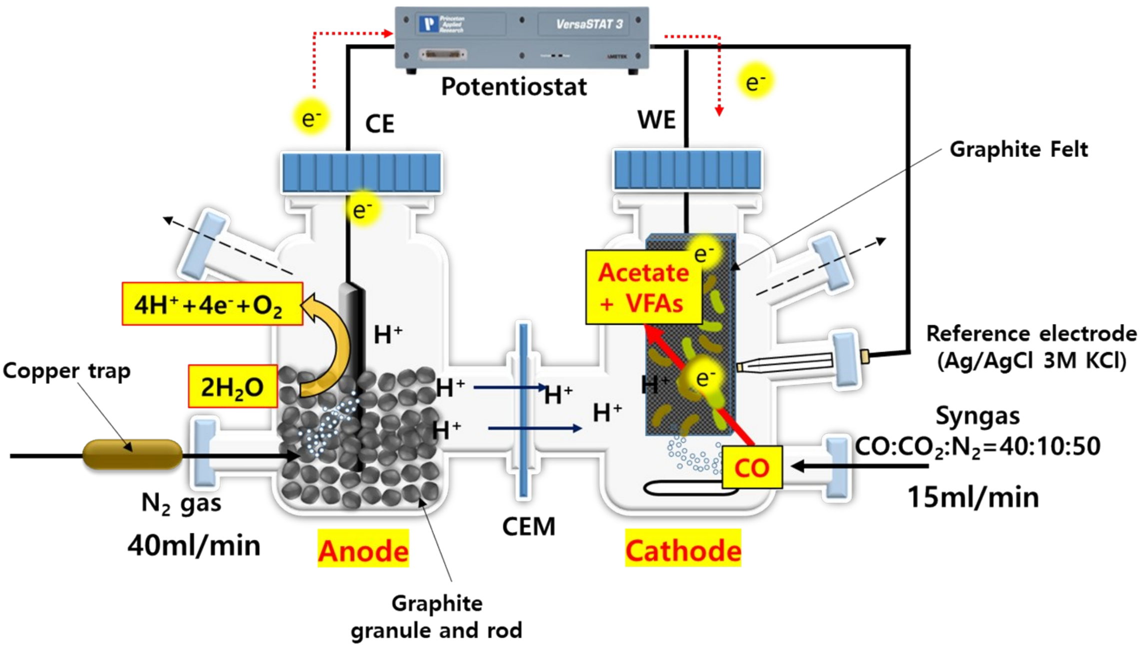

Fig S1. Configuration of the BES reactor

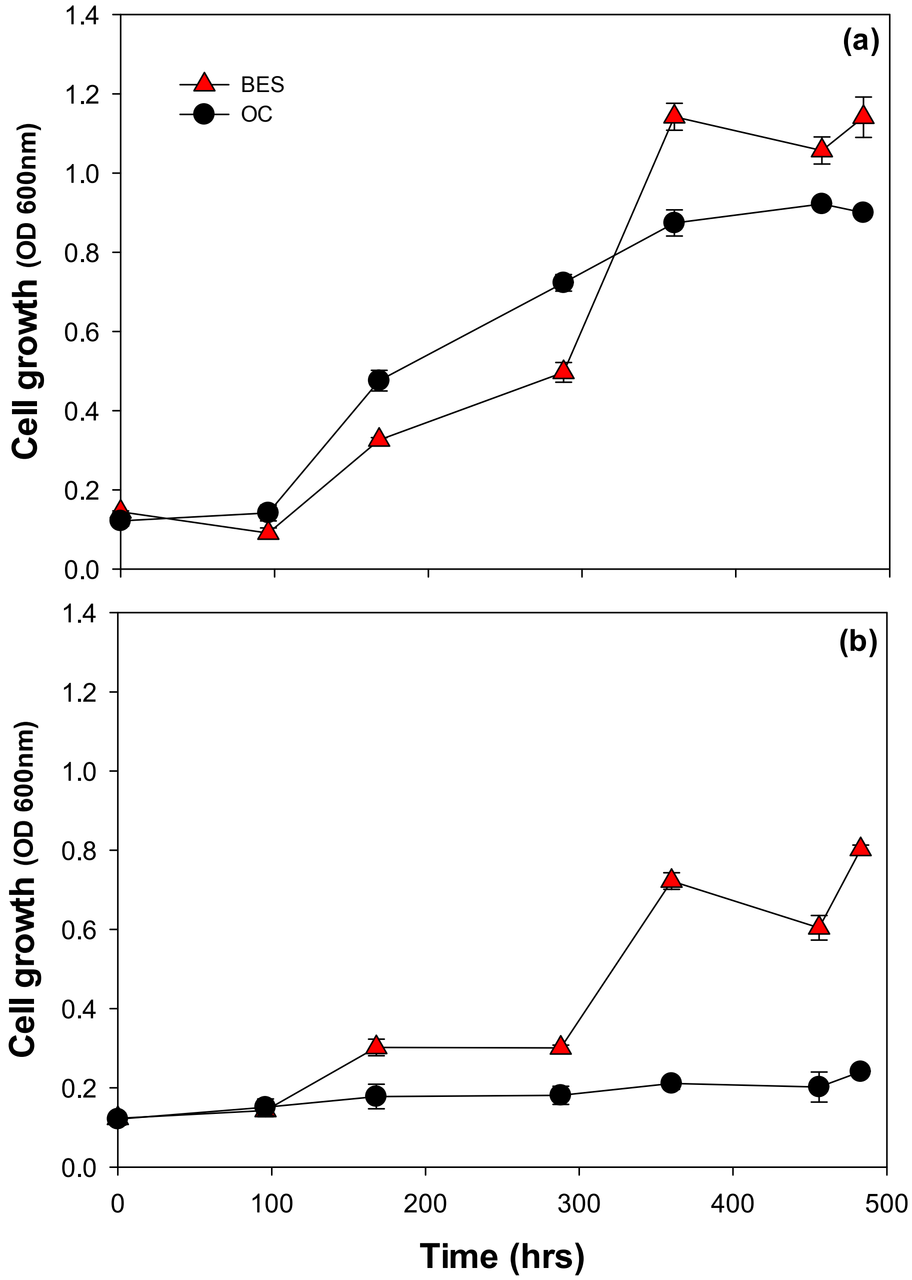

Fig S2. Comparison of cell growth between the BES culture and open circuit culture (control). (a) with the yeast extract, (b) without the yeast extract.

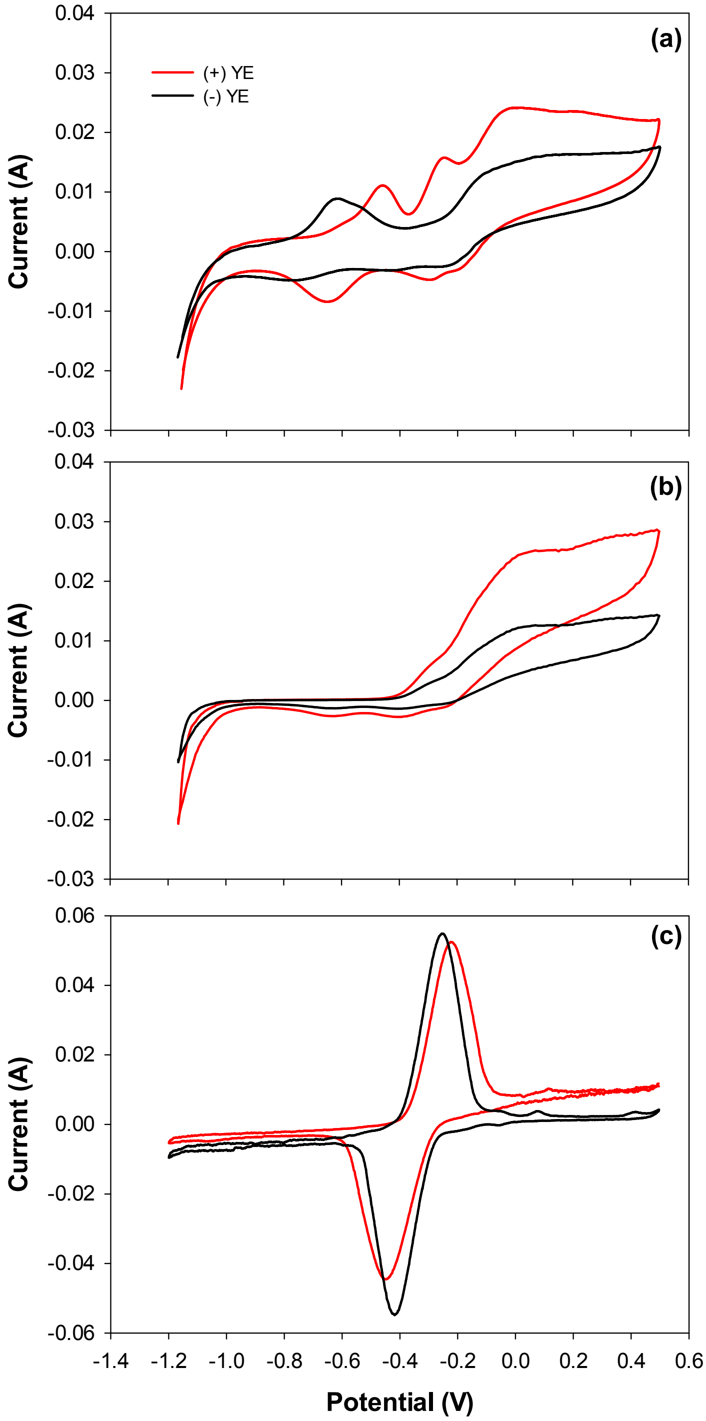

Fig S3. Comparison of the electrochemical reaction by cyclic voltammetry in (a) a BES with -1.1V vs. Ag/AgCl, (b) BES with an open circuit mode, (c) abiotic control with HNQ only.

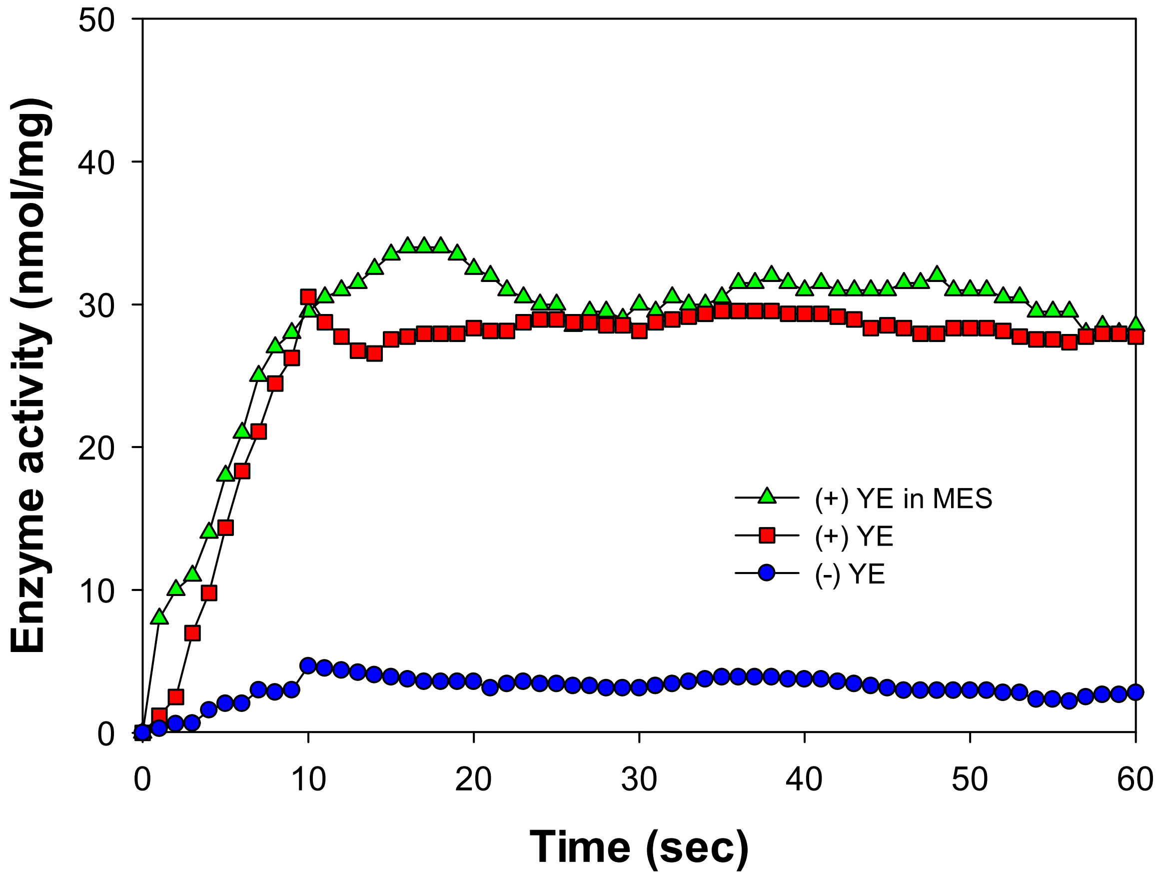

Fig S4. Change of CODH enzyme activity of the crude cell lysate in serum bottle and MES according to measurement time.

References

1. P. Parthasarathy and K. S. Narayanan, *Renewable Energy*, 2014, **66**, 570-579.