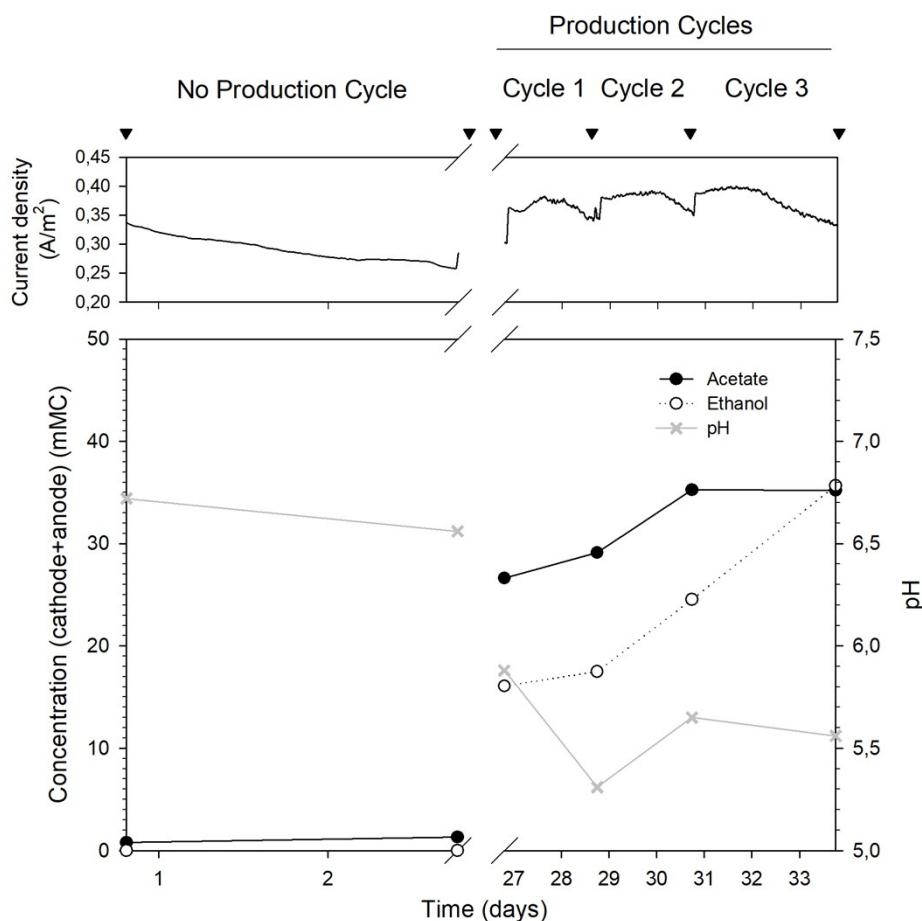


### Electronic supplementary information (ESI)

**Fig. S1** Current signal, pH and total concentration of acetate and ethanol in the reactor 1. Black inverted triangles on the top part of the figure indicate sampling and subsequent flushing with CO<sub>2</sub>.



**Table S.1.** Composition of the modified ATCC1754 ETC medium used in the BES reactors.

Medium component	(g L <sup>-1</sup> )	Trace metal solution component	(mg L <sup>-1</sup> )	Vitamin solution component	(μg L <sup>-1</sup> )
KH <sub>2</sub> PO <sub>4</sub>	0.1	Nitrilotriacetic acid	20.0	Biotin	20.0
NaCl	0.8	MnSO <sub>4</sub> ·H <sub>2</sub> O	10.0	Folic acid	20.0
NH <sub>4</sub> Cl	1.0	Fe(SO <sub>4</sub> ) <sub>2</sub> (NH <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	8.0	Pyridoxine hydrochloride	100.0
MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.2	CoCl <sub>2</sub> ·6H <sub>2</sub> O	2.0	Thiamine hydrochloride	50.0
KCl	0.1	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	0.002	Riboflavin	50.0
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.02	CuCl <sub>2</sub> ·2H <sub>2</sub> O	0.2	Nicotinic acid	50.0
MES	1.95	NiCl <sub>2</sub> ·2H <sub>2</sub> O	0.2	DL- calcium pantothenate	50.0
Cysteine HCl	0.4	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	0.2	Vitamin B12	1.0
		Na <sub>2</sub> SeO <sub>4</sub>	0.2	p-aminobenzoic acid	50.0
		Na <sub>2</sub> WO <sub>4</sub>	0.2	Lipoic acid (Thioctic acid)	50.0



**Table S.2.** Overview of the main features and performance of ethanol-producing biocathodes fed with CO<sub>2</sub> as the sole carbon source.

Voltage (V vs. SHE)	T (°C)	pH	Inoculum	Feeding	Products	Maximum [ethanol] (mmol C ethanol)	Maximum Ethanol-to- acetate ratio (**)	Ref.
-0.9	30	7.0-4.5	Anaerobic sludge	20:80 (CO <sub>2</sub> :N <sub>2</sub> )	Acetate, butyrate, ethanol	2.56	<1	1
-0.8/-0.9	37	7.0	Anaerobic sludge + <i>C. ljungdahlii</i>	80:20 (CO <sub>2</sub> :N <sub>2</sub> )	Acetate, butyrate, ethanol	21.71	<1	2
-0.69	25	<5.0	<i>Sporomusa ovata</i> DSM-2662	80:20 (CO <sub>2</sub> :N <sub>2</sub> )	Acetate, ethanol	26.3	<1	3
-0.40	30	7.3	Anaerobic bog sediment	80:20 (CO <sub>2</sub> :N <sub>2</sub> )	Butanol, ethanol, acetate, propionate, butyrate	0.7	<1 (0.084)	4
-0.6	30	7.0	Enriched homoacetogenic consortia	20:80 (CO <sub>2</sub> :N <sub>2</sub> )	Acetate, ethanol	3.52	<1	5
-50 mA / -5 A·m <sup>-2</sup> (*)	30	7.6-5.0	Anodic effluent of a MFC and a UASB digesting microalgae (1:1)	90:10 (N <sub>2</sub> :CO <sub>2</sub> )	Butyrate, isopropanol, ethanol, acetate, formate, propionate, acetone	11.72	<1	6
-0.8	38	4.2-6.3	Carboxydrotrophic mixed culture (dominated by <i>Clostridium</i> spp.)	CO <sub>2</sub>	Acetate, butyrate, ethanol, butanol	20.4	<1 (0.522)	7
-0.8	29	6.0	Mixed culture obtained from corroded metal surface	CO <sub>2</sub>	Acetate, butyrate, propionate, ethanol, butanol, methanol	n.r.	<1	8
-0.8	29	8.0–4.36	Mixed culture obtained from corroded metal surface	CO <sub>2</sub>	Methanol, ethanol, butanol, acetate, butyrate, formic acid	n.r.	>1	9
-0.8	35	4.9-5.2	Mixed culture obtained from a BES performing acetotogenesis from bicarbonate	CO <sub>2</sub>	Acetate, butyrate, isobutyrate, caproate, ethanol, butanol, isobutanol, hexanol	56.1	<1	10
-0.8	25	7.0-5.3	Enriched culture of Isolate I-19	CO <sub>2</sub>	Acetate, ethanol	35.65	>1 (1.54)	This study

\*: fixed reducing current; \*\*: calculated with the maximum of ethanol and acetate reported; n.r.: not reported.

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