

Supplementary information

S1. MES setup diagram

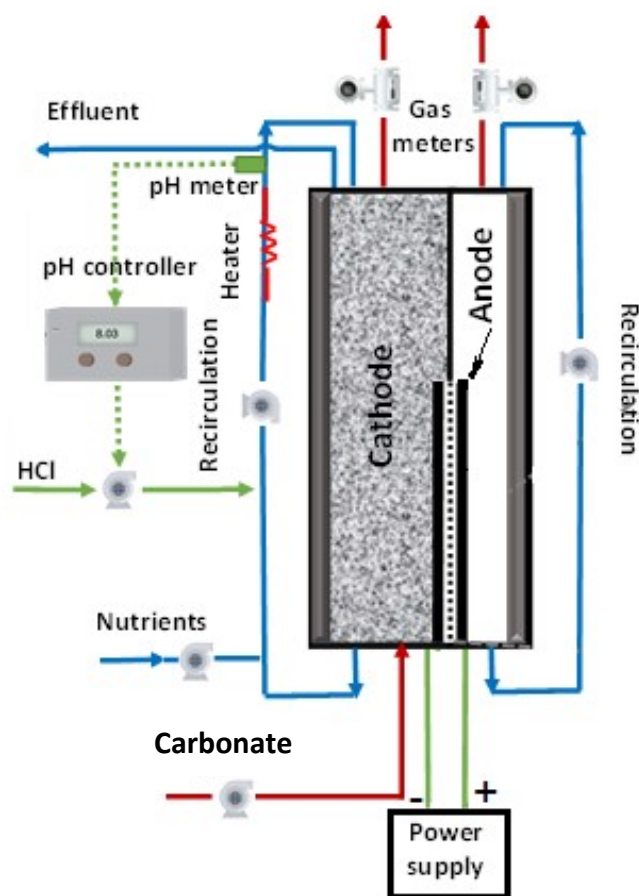


Figure S1. Schematic representation of a MES cell with continuous carbonate supply. The dotted line denotes PEM. Figure adapted from Gomez Vidales et al³⁷.

S2. Energy consumption and coulombic efficiency calculation

The energy consumption (E_{H_2}), per litre of equivalent hydrogen ($Wh L_{H_2}^{-1}$), and the Coulombic efficiency (CE) were determined as follows:

$$E_{H_2} = \frac{VIt}{\sum_i v_i Q_i} \quad (1)$$

$$CE (\%) = \frac{FN \sum_i n_i C_i}{\int_{t=0}^t Idt} 100, \quad (2)$$

where V is the voltage (V), I is the current (A), and t is the time (day). Q_i is the flow rate of cathodic products ($L d^{-1}$), i is the cathodic product (i.e., CH_4 , H_2 , acetate), and v_i represents the stoichiometric amount of H_2 necessary to form the given products ($mol mol^{-1}$), which is 4 for both CH_4 and acetate. For Equation. (2), F is the Faraday constant ($96485 C mol^{-1}$), while N is the total amount of cathodic products (in mol), n_i defines the equivalent mole of electron required per mole of generated i -th product (n_i is 2 for H_2 generation and 8 for CH_4 and acetate), and C_i delineates the mole fraction of i in the product ($mol mol^{-1}$).

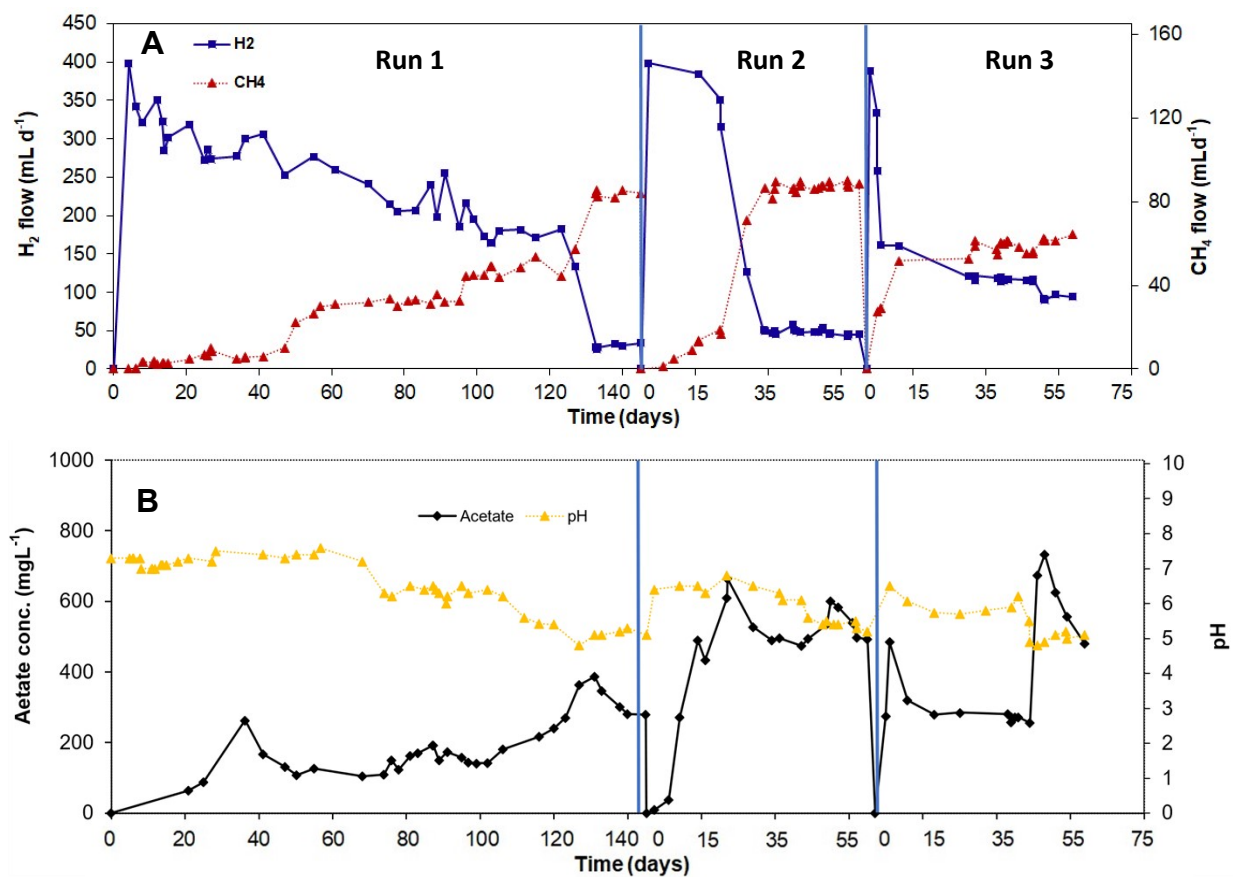


Figure S2: Time dependence of (A) CH_4 and H_2 production rate, (B) Acetate concentration and pH in the cathode compartment of MES-1 cell.

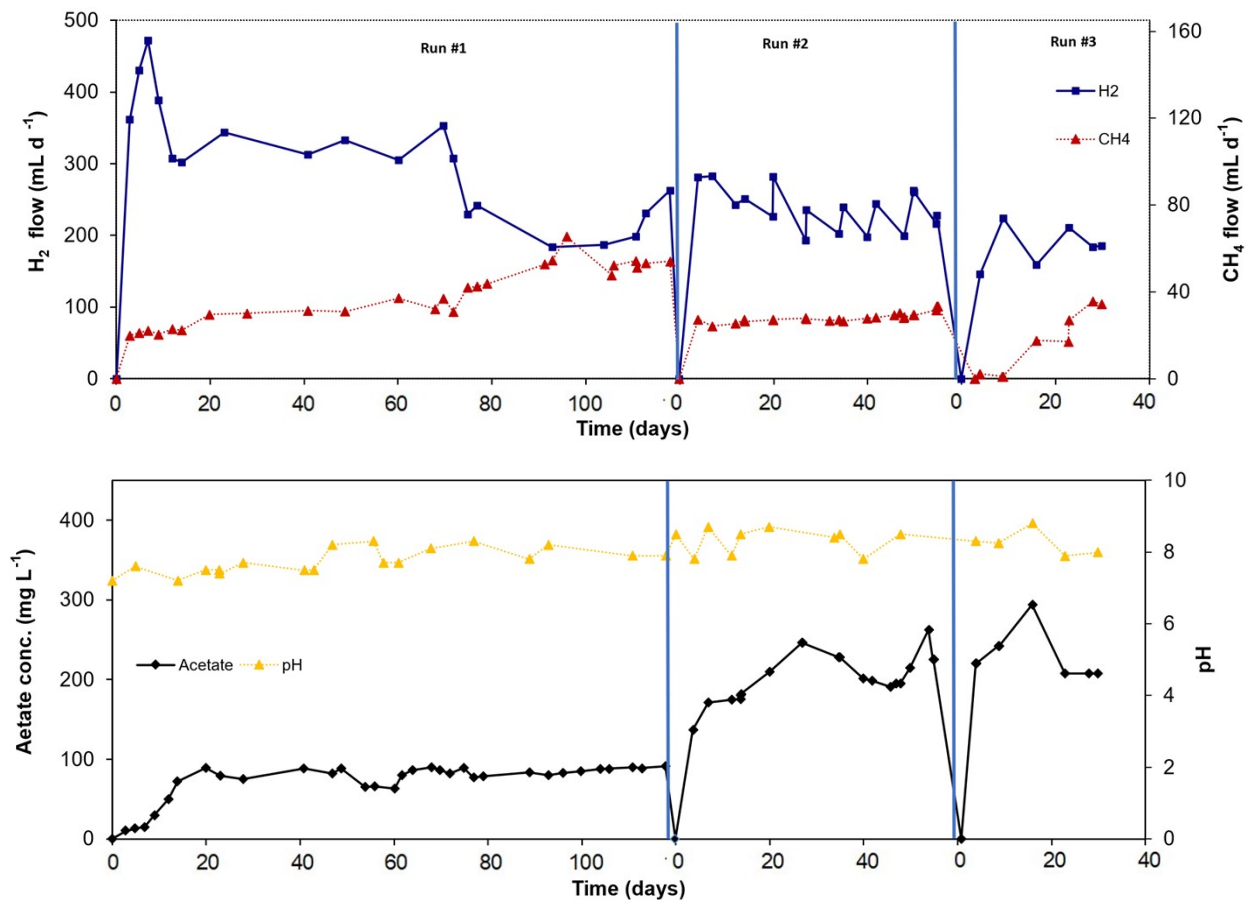


Figure S3: Time dependence of (A) CH_4 and H_2 production rate, (B) Acetate concentration and pH in the cathode compartment of MES-2 cell.