Electrochemical system for wastewater treatment and low voltage water electrolysis decoupling hydrogen production using bioelectrochemical system

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**Highlights**

* Hydrogen generation coupling Electrolyser with MFC device
* Hydrogen production with only 1 V of cell voltage
* Wastewater valorization

**1. Introduction**

Wastewater is a huge reservoir of biomass energy already collected but still generating more costs than added-value products. Microbial electrochemistry technology development is a real opportunity to take advantage of this energy source. Freshly we have validated the proof of concept of an innovative device associating a bioelectrochemical system and a decoupled water electrolysis in order to produce hydrogen [1]. This architecture consists of two reactors running separately linked through a redox mediator cycle : i) a Microbial Fuel Cell (MFC) cascade system which oxidates wastewater while reducing potassium hexacyanoferrite ii) an electrolysis cell using a semipermeable separator which produces H2 while regenerating the mediator.

*,***2. Methods**

Microbial fuel cell (MFC) is a spontaneous electrochemical process that allows current recovery between two reactions: acetate oxidation at the anode and HCF(III) reduction at the cathode.

$C\_{2}H\_{3}O\_{2}^{-}+4H\_{2}O\rightarrow 2HCO\_{3}^{-}+9H^{+}+8e^{-}$ (1)

$\left[Fe(CN)\_{6}\right]^{3-}+e^{-}\rightarrow \left[Fe(CN)\_{6}\right]^{4-}$ (2)

In the electrolyser, two reactions occur at anode electrode, the HCF(II) oxidation and the water reduction in the catholyte solution. The anolyte pH must be maintained to high values (alkaline) to avoid an acidic reaction on HCF (II). In addition, NaH2PO4 buffer solution is employed and K2SO4 salt is added to increase ionic conductivity. Therefore, catholyte had the similar pH value and similar buffer composition.

[Fe(CN)6]4- → [Fe(CN)6]3- + e- (3)

According to De Silva Munoz et al. [2] two steps of electrochemical reduction are possible in phosphate buffer:

$H\_{2}PO\_{4}^{-}+e^{-}\rightarrow H\_{ad} +HPO\_{4}^{2-}$ (4)

$e^{-}+H\_{ad} + H\_{2}PO\_{4}^{-}\rightarrow H\_{2}+HPO\_{4}^{2-}$ (5)

And the acid-base equilibrium:

$HPO\_{4}^{2-}+H\_{2}O\rightarrow H\_{2}PO\_{4}^{-}+OH^{-}$ (6)

With the acid-base equilibrium leads to water reduction as follow:

$2H\_{2}O+2e^{-} \rightarrow H\_{2}+2OH^{-}$ (7)

**3. Results and discussion**

On one hand, organics acid oxidation is coupled to HCF(III) reduction. On the other hand, oxidation of HCF(II) is coupled to water splitting. HCF couple appears to be an interesting opportunity as a mediator in electrolyser for several reasons : i) a low overpotential at low current density which will overcome MFC system limitation using oxygen reduction reaction; ii) a low thermodynamic redox potential which reduces energy costs for water splitting (vs anodic water oxidation); iii) a high reversibility and stability which justifies its wide use in electrochemical system. The aim of this work is to validate the feasibility of such coupled systems as a proof of concept. Using a simple architecture, our MFC cascade system fed with glucose produces a current density up to 1.9 A.m-2 (with a COD removal rate of 30 mol.m-2.d-1 and a HCF(III) reduction rate of 8.9 mol.m-2.d-1).

**4. Conclusions**

The apparatus can lead to hydrogen production by water electrolysis at cell potential below 1V with a current density up to 30 mA.cm-2. This technology offers new perspectives for microbial electrochemistry technology development while limiting several bottleneck of direct energy recovery using microbial electroactivity. Decoupling hydrogen production and biocatalyzed biowaste oxidation permits to i) avoid oxygen reduction reaction limitations in both units, ii) produce energy vector in low cost reactor ant to yield high rate hydrogen in usual electrolyzer. In order to propose low cost system, we have developed mediator electrolyser using carbon and stainless steel electrodes.

**References**

1. Belleville et al. International Journal of Hydrogen Energy, 43, 14867, 2018
2. De Silva Munoz et al. International Journal of Hydrogen Energy, 35,8561, 20 0